Studies on Novel Flame Retardants and Their Applications in Polymers

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Studies on Novel Flame Retardants and Their Applications in Polymers

(新型の難燃剤及びポリマーへの応用)

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Abstract

Epoxy resin is a kind of high performance polymer materials. Epoxy resin based composites are widely applied in various areas due to their low cost, ease of fabrication. However, the commonly-used epoxy resins are consists mainly of carbon, hydrogen and oxygen atoms, therefore, there are some shortages, such as, the high flammability and low thermal stability at elevated temperatures. In order to enhance the flame resistance of epoxy resin, flame retarded epoxy resins were prepared by adding additive halogen free flame retardants or reactive flame retardants. In recent years, much more reports were published to synthesis novel high performance flame retardants by putting halogen-free flame retarded functional groups, functional modification or designing & synthesizing combination agents integrating flame retardance and curing feature. In this paper, some compound flame retardants and novel flame retardants were designed and synthesized to enhance the flame resistance and mechanical performance of flame retarded polymer composites.

In the second chapter, microencapsulated red phosphorous (MRP) was synthesized by using melamine-formaldehyde resin through in-situ polymerization, and used as a synergistic agent of magnesium hydroxide (MH) and aluminium hydroxide (ATH) for flame retarded polyethylene (PE), the best proportion and performance of three flame retardants was studied in detail. Results showed that the best compound flame retardant composed of MH, ATH and MRP with the weight ratio of 46/46/8, and the flame retarded PE had a better combination performance when filling with 45 wt% compound flame retardants aboved. In order to improve the mechanical performance

loss of composite when filled with high fraction of inorganic flame retardants, two polymeric compatibilizers Polyolyaltha Olfin-grafting-maleic anhydride (POE-g-MAH) and Ethylene-Propylene-Diene Monomer-grafting-maleic anhydride (EPDM-g-MAH) were selected to toughen the flame retarded PE composite. Results showed the flame resistance and mechanical properties of composites improved greatly with an increase of compatibilizer content, under the same loading condition, POE-g-MAH has a better contribution on the flame resistance and EPDM-g-MAH has a better toughening effect. Considering the cost/performance ratio, the best flame retarded PE composite can be obtained by filling with 45 wt% compound flame retardants and 10 wt% EPDM-g-MAH.

In the third chapter, a novel phosphorous-containning flame retardant and hardene raryl phosphinate dianhydride BPAODOPE was synthesized and its structure was identified by FTIR and ^{1}H-NMR. BPAODOPE was used as flame retardant and hardener for preparing halogen-free flameretarded epoxy resins when coupled with another curing agent. Thermal stability, morphology of char layer, flame resistance and mechanical properties of flame-retarded epoxy resins were investigated by thermogravimetric analysis, SEM, limiting oxygen index (LOI), UL 94 test, tensile, and charpy impact test. The results showed that the BPAODOPE had a better flame resistance, the flame resistance and char yield of flame-retarded epoxy resins increased with an increase of phosphorus content, tensile strength and impact strength of samples gradually decreased with an increase of BPAODOPE. The flame retarded sample with phosphorus contents of 1.75% showed the best combination properties, LOI value was 29.3, and the vertical burning reached UL 94 V-0 rating, tensile strength and impact strength were 30.78 Mpa and 3.53 kJ/m^2, respectively.

In the fourth chapter, another novel phosphorus containning flame retardant & curing agent PES was synthesized successfully with pentaerythritol, phosphorus oxychloride and ethylenediamine, the structure and performance of production was characterized by fourier transform infrared spectrum (FTIR), nuclear magnetic resonance (^{1}HNMR), mass spectro metry (ESI-MS) and thermogravimetric analysis (TGA). The synthesized PES and commercial DDS was used as flame retardant and curing agent, and the flame retarded epoxy resin composites were prepared with different phosphorus content. The results showed that the initial decomposition temperature of flame retarded epoxy resin composite decreased gradually with an increase of phosphorus content, when the phosphorus content was 3.48%, the LOI value was 28.9, reached the UL 94 V-0 rating, tensile strength and impact strength were 62.76 MPa and 6.81kJ/m^2 respectively.

In the fifth chapter, an intumescent flame retardant containing phosphorus and nitrogen PDEPDM was synthesized successfully by using phenyl phosphonic dichloride melamine, bisphenol A, triethylamine and dichloromethane through three step reactions, and the suitable reaction conditions were tested under different reaction temperature, reaction time and solvent ratio. As-synthesized PDEPDM was characterized by the FTIR, ^{1}HNMR and ^{31}PNMR. The flame resistance of the PDEPDM in Polyethylene (PE) was investigated by LOI and UL 94 test. Under the optimal content of 32 wt% PDEPDM in PE, the LOI was 29.8 and reached UL 94 V-0 rating, tensile strength and impact strength were 10.06 MPa and 16.77 kJ/m^2 respectively.

In the sixth chapter, a novel P and N containing intumescent flame retardant and curing agent PMXSPB was synthesized and used as a flame retardant and curing agent for preparing flame retarded EP resin composites. The thermal stability, mechanical

properties, flame resistance, and morphology of the char layer of flame-retarded EP resins were investigated using thermogravimetric analysis, tensile and Charpy impact tests, limiting oxygen index (LOI), UL 94 test and SEM, respectively. The results demonstrated that the flame resistance and the residual char ratio at 600℃ of EP composites improved significantly with an addition of PMXSPB. The flame retarded EP composites filling with the phosphorus content of 3.01% (EP 100 g and PMXSPB 35 g) exhibited the best combination of properties, LOI was 31.2, vertical burning test reached UL 94 V-0 rating, and the tensile and impact strengths were 51 MPa and 4.8 kJ/m^2, respectively.

In the seventh chapter, a novel flame retardant (PPSDB) containing phosphorus, nitrogen and boron was synthesized and its chemical structure was confirmed by FTIR and ^{1}HNMR. As a new intumescent flame retardant for polyethylene (PE), the thermal stability of PPSDB was confirmed to suit for the requirement for fabricating PE composites by TGA. The flame retardant PE (PE/PPSDB) composites were prepared by filling PPSDB with different fractions. The PE/PPSDB composites showed a good flame resistance, antidripping properties and compatibility with matrix resin. The PE/PPSDB composite with 30 wt% PPSDB had the best combination properties; the limited oxygen index (LOI) value was 29.2, and vertical burning reached UL 94 V-0 rating, the tensile strength and notched impact strength were 18.6 MPa and 12.5 kJ/m^2, respectively. The morphologies of residual char showed a lot of protruding structures consisting of smaller protuberances, which prevented the combustion of composite and enhanced anti-dripping property effectively.

Contents

Abbreviation

The abbreviation of chemical substances：

PE: Polyethylene

MH: Magnesium Hydroxide

ATH: AluminiumHydroxide

MAH: Maleic Anhydride

POE: Polyolefin Elastomer

EPDM: Ethylene Propylene Diene Monomer

POE-g-MAH: Maleic Anhydride functionalized Polyolefin Elastomer

EPDM-g-MAH: Maleic Anhydride functionalizedEthylene Propylene Diene Monomer

RP: Red Phosphorous

MRP: HereinMicroencapsulated Red Phosphorous

IFR: Intumescent Flame Retardant

ODOPB: 2-(6-oxid-6H-dibenz<c,e><1,2>oxaphosphorin-6-yl)-1,4-benzenediol

TMAC: Trimellitic anhydride acid chloride

DOPO: 9,10-dihydro-oxa-10-phosphaphenanthrene-10-oxide

BPAODOPE:dianhydride1,4-bis(phthalicanhydride-4-carbonyl)-2-(6-oxido-6H-dibenz [c, e][1,2]-oxaphosphorin-6-yl)-phenyleneester

DGEBA(E-51): Bisphenol A type epoxy resin

EP: Epoxy Resin

MeHHPA: Methylhexahydrophthalic anhydride

BDMA: N-Benzyldimethylamine

PER: Pentaerythritol

DDS: 4,4-diamino Diphenyl Sulfone

TEA: Triethylamine

ACN: Acetonitrile

DMAP: 4-dimethylaminopyridine

AGE: Allyl glaycidyl ether

SPDPC: Spirocyclicpentaerythritolbisphosphoratedisphosphorylchloride

PES: Poly Diamine Amine Pentaerythritol Phosphate

MCA: Melamine Cyanurate

BPA: Bisphenol A

PPD: Phenyl PhosphonicDichloride

MA: Melamine

TA: Triethylamine

AI: Acetonitrile

DCM: Dichloromethane

PDPPE: phenyl phosphinic arid di-4-[1-(4-pheny phodphonic acidmonophenyl ester-yl)-methyl-ethyl]Bisphenol A

PDCEPE: phenyl phosphinic arid di-4-[1-(4-pheny phodphonic acidmonophenyl ester-yl)-methyl-ethyl]Phenylphosphonic dichloride

PDEPDM: phenyl phosphinic arid di-4-[1-(4-pheny phodphonic acidmonophenyl ester-yl)-methyl-ethyl]pheny ester dimelaminium

PMXSPB: poly-(meta-xylylenediaminespirocyclic pentaerythritol bisphosphonate)

MXDA: m-Xylylenediamine

THF: Tetrahydrofuran

PPC: PhenylphosphonicDichloride

DEAB: DiethanolamineBorate

PPSDB: poly(phenylphosphamidespirocyclicdiethanolamine borate)

The abbreviation of Characterization：

XPS: X-ray photoelectron spectroscopy

SEM: Scanning electron microscope

LOI: Limiting oxygen index

UL 94 test: Vertical burning

FTIR: Fourier transform infrared spectrometer

^{1}H NMR: Proton Nuclear Magnetic Resonance Spectra

TGA: Thermal Gravimetric Analysis

DTG: Differential Thermal Gravity

DSC: Differential Scanning Calorimetry

ESI-MS: Electrospray Ionization Mass Spectrometry

Chapter 1

Introduction

1.1 The advantages and shortages of epoxy resins

Epoxy resin is a kind of high performance organic polymer materials [1-3] which possess reactive oxirane moieties readily available for crosslinking either under catalytic homopolymerization conditions or in the presence of active hydrogen containing molecules as curing agents, such as amides or polyfunctional amines, acids, phenols, thiols, etc. Accordingly, after curing, the infusible thermoset polymers are obtained. These epoxy resin based composites are widely applied in various areas due to their low cost, ease of fabrication and highly attractive physico-chemical and mechanical characteristics, such as electronics, transportation and aerospace industry, adhesives, composites, paints, protective surface coatings, laminates, encapsulates for semiconductors and electronic devices [4-6].

1.1.1 The advantages of epoxy resin

(1) Higher mechanical performance

There is stronger cohesive force for the compact molecular structures of epoxy, so their mechanical performances are higher than the phenolic resins and unsaturated polyester resins.

(2) Stronger cohesive force

Due to the large amount of active epoxy groups and polarity groups, such as, hydroxy and ether bonds, amine bonds, ester bonds etc, those groups endow the epoxy

curing composite with an excellent cohesive force for some polarity based materials, such as, metals, ceramics, glasses, concretes and woods etc.

(3) Lower curing shinkage rate

The curing shinkage rate of epoxy resin (1%~2%) is almost the smallest one among those thermoset polymers, such as, the curing shinkage rate of phenolic resin is 8%~10%，unsaturated polyester resins is about 4%~6%, organic silicane resin is 4%~8%. Moreover, the parameter of linear expansion of epoxy resin is as smaller as 6×10^{-5}/℃. Therefore, the volume change of epoxy resin is not evident after cured.

(4) Better machinability

No smaller molecules volatile matters will be produced during the curing process of epoxy resin, so, the low pressure molding or contact pressure molding can be adopted for preparing epoxy productions. All kinds of envionmental friendly coatings including solvent-free, high solid contents, powders, or water-based paints can be easily produced by mixing different curing agents with epoxy resin.

(5) The excellent electrical insulating properties

The dielectrical property of the epoxy resin is the best one among thermoset polymers, it is often applied as electronic packaging materials.

(6) The excellent stability and chemicals resistance

The storage life of epoxy resin is one year when the resin is sealed tightly in dry and low temperature, just for its excellent stability. Furthermore, the epoxy resin has special chemical stability. The alkali, acid and salt resistance of epoxy resin is better

than phenolic resin and unsaturated polyester resin. Therefore, the epoxy resin can be used as anti-corrosion undercoat. Because of the special three-dimensional networks structure of epoxy curing composite, it can resist the immersion in oil, so it can also be used as the insidewall lining material for oil tank, ships or planes

1.1.2 The shortages of epoxy resin

However, the commonly-used epoxy resins are consists mainly of carbon, hydrogen and oxygen atoms, therefore, there are some shortages, the high flammability and low thermal stability at elevated temperatures [7-9]. Another, poor weather ability for the aromatic ether bonds, these bonds will be degraded and broken when endured in solar exposure, so the bisphenol A type epoxy resin can not be used as the surface coating for outdoor productions. In order to avoid the risk of fire, the flame retarded epoxy resin composites are needed in much more circumstances. In this thesis, some novel flame retardants will be synthesized for preparing flame retarded epoxy resin composites.

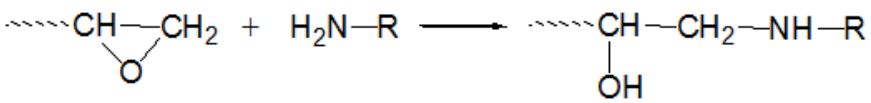
1.2 The curing reactions and curing agents of epoxy resins

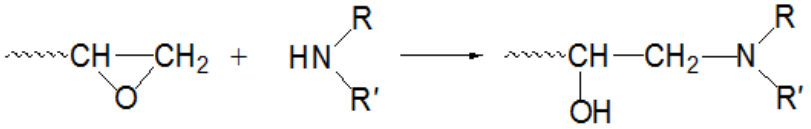
1.2.1 The reactions of epoxy resin

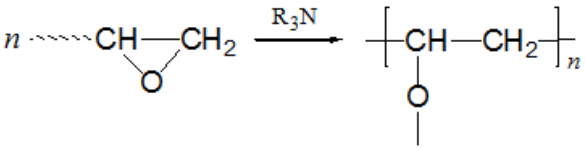
The activity of epoxy resin is rather stable, the bisphenol A type epoxy resin will not change its structure when heated to 200 ℃. However, the active epoxy groups in epoxy resin will react with curing agent to generate net-like macromolecules, and the main reactions are decided by the epoxy and hyroxy groups in their structures.

(1) The reaction between epoxy and reactive hydrogen containing compounds

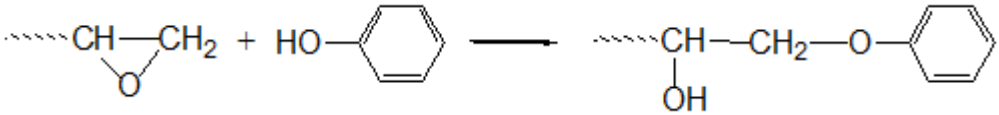
The epoxy group can react with primary amine and secondary amine easily, but it can not react with teriary amine, it can catalyze the ring open reaction of epoxy, polymerize the epoxy resin. The specific chemical reaction processes are listed as following. Therefore, the compounds containning tertiary amine can also be used as the curing agent for epoxy resin.



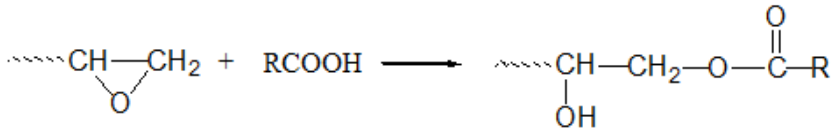




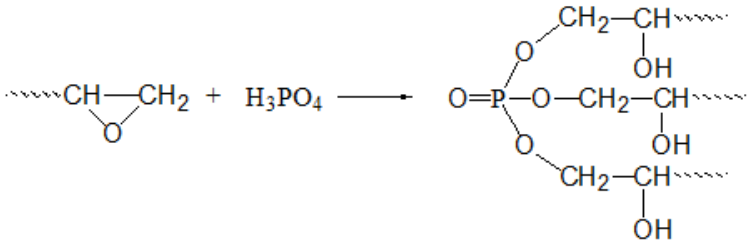
(2) The reaction between epoxy and phenols



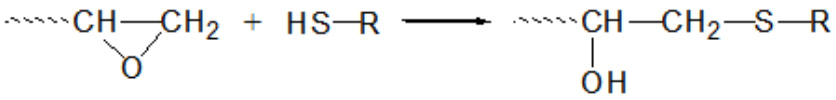
(3) The reaction between epoxy and carboxylic acid



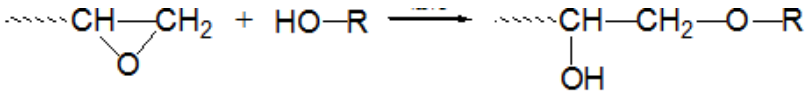
(4) The reaction between epoxy and inorganic acid



(5) The reaction between epoxy and mercapto group

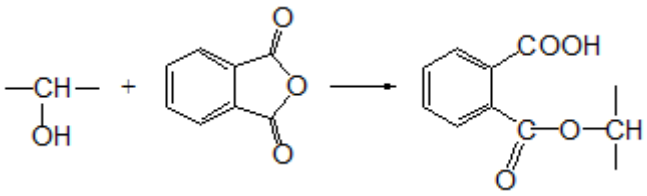


(6) The reaction between epoxy and alcoholic hydroxyl group

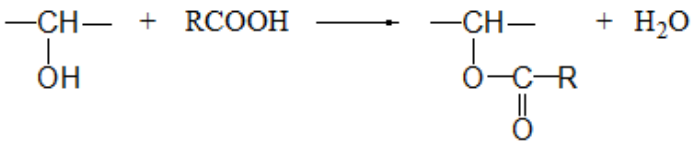


1.2.2 The reactions of hydroxyl in epoxy resin

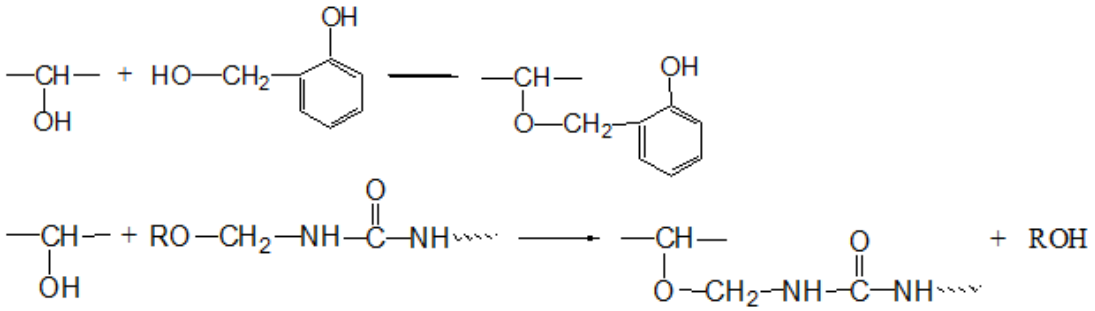
(1) The reaction between hydroxyl with acid anhydride



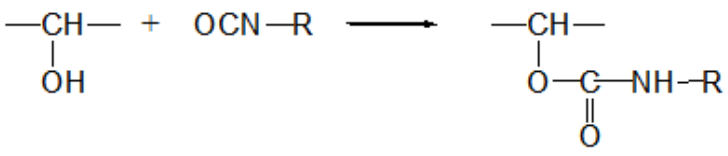
(2) The reaction between hydroxyl with carboxylic acid



(3) The reaction between hydroxyl with hydroxymethyl or alkoxy



(4) The reaction between hydroxyl with isocyanate



(5) The reaction between hydroxyl with silanol or its alkoxy, it is shown in Fig.1.1.

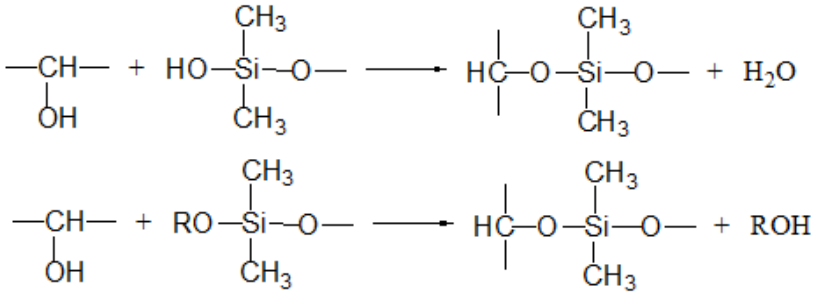


Fig.1.1 The reaction of hydroxyl and silanol

1.2.3 The curing agents for epoxy resin

The curing reaction of epoxy resin is driven by adding curing agents, the reaction can be achieved through the reaction between some groups in curing agent with epoxy or hydroxyl in epoxy resin. There are a great variety of curing agents, according to the different chemical compositions and structures, the curing agents can be divided into amine curing agent, anhydride curing agent, synthetic resin type curing agent, and polysulfide rubber type curing agent, and amine and anhydride curing agents are most commonly used productions.

(1) Amine curing agent

Amine curing agents include polyamine, tertiary amine and imidazole, boron amine and boron amine complex curing agents.

(2) Anhydride curing agents

The advantages of anhydride curing agents are less skin imitation, higher performance of cured materials, excellent dielectric properties, especially for the application in the field of electrical insulation. The shortages are higher curing temperature, longer curing period, etc.

1.3 The preparation of flame retarded epoxy resins

In order to improve the flame resistance of epoxy resin, we can put some flame retardants into epoxy system or synthesizing novel epoxy resin containning flame retardant functional groups, that is, some inorganics or organics containing flame retardant elements can be selected as effective flame retardants, such as N, P, Sb, Cl, Br, B, Al, and Si etc.

Additive flame retardants [10, 11]: some flame retardants, such as halides, red phosphorous, aluminium hydroxide, magnesium hydroxide, zinc borate, phosphates and ammonium polyphosphate etc, can be physically added into liquid epoxy resin and cured for flame retarded epoxy composite, this method has some advantages, such as, economic, easily doing, fast and simple. However, the produced composites by this way have poor mechanical properties for bad compatibility, the powders will be oozed out, the surface features will be affected when used for long time. Therefore, in order to solve these problems, researchers attempted to refine the powders of flame retardant or modify the powder surface with coupling agents, and aimed to improve the compatibility between powders and liquid epoxy resin.

Reactive flame retardant[12, 13]: that is synthesizing flame retarded epoxy resin or curing agent by designing new molecular structure, and integrating structure unit with flame resistance into the main chains or side chains of epoxy resin. This kind of flame retardants include halogen based, nitrogen based, phosphorous based and silicon based flame retardants, and the Cl, Br containning flame retardants are the largest production in the whole world, they are widely used in the electronics and electrical equipments fields. However, the halogen-containning flame retardants will produce large amount of toxic gas when in use or recycling, pollute the envionment, so it is

necessary to develop new low smoke, low toxic and halogen free envionmental flame retardants and flame retarded polymers to replace the halogen flame retardants. As for the halogen free flame retardants, the nitrogen flame retardant has a low flame retardant efficiency, while it is very difficult to synthesize the silicon flame retardant, and its relative flame retardant mechanism is not very clear up to now. Therefore, the reseach topic mainly focused on the phosphorous flame retardants in recent years, and the phosphorous containning curing agents are getting to be more and more popular.

1.4 The mechanism of flame retardance

As is well known, the three factors of burning include combustible substances, oxygen gas and certain temperature, each factor is necessary for burning. Therefore, the flame resistance mechanism of flame retardants is to suppress one or two aboved factors, to prevent or slow down the burning. The specific flame resistance mechanisms are different for different flame retardants, it can divides into physical effect and chemical effect, the physical effect is corresponding to the heat absorption, dilution of combustible substances and isolation of air; and the chemical effect is related to charring, elimination free radicals and phosphorylation effect, etc [14].

The combustion of solid substances such as polymer materials can be divided into three stages: (a) substances decompose when heated to high temperature and produce combustible gas; (b) these combustible substances can be burned further; (3) the heat from combustion induce the solid substances or molten state substances decompose further, sustain the combustion. If one or two stages above are suspended, it will endow the materials with flame resistance through gaseous phase flame resistance, condensed phase flame resistance or interruptive heat exchange etc.

(1) Mechanism of gaseous phase flame resistance

The chain reaction of free radicals can be occurred in the flame, such as,

$$\cdot OH+CO \rightarrow CO_2+\cdot H$$

$$\cdot OH+RCH_3 \rightarrow RCH_2\cdot+H_2O$$

$$RCH_2\cdot+O_2 \rightarrow RCHO+\cdot OH$$

$$\cdot H+O_2 \rightarrow \cdot OH+\cdot O\cdot$$

Gaseous phase flame resistance refers to the flame resistance occurance in the gaseous phase, that is, the combustion reactions of combustible gases can be suspended or retarded in gas phase, the gaseous phase flame resistance often includes the following circumstances:

(a) When the flame retardants were heated, the free radicals can be produced to capture thechain growth during combustion reaction. Currently, widely used halogen flame retardants and halogen-antimony synergy system are the typical gaseous phase flame resistance. The halogen flame retardant decomposed at higher temperature and released HX, HX will react with free radicals in flame as the following process：

$$HX+\cdot OH \rightarrow H_2O+\cdot X$$

$$HX+\cdot O\cdot \rightarrow \cdot OH+\cdot X$$

$$HX+H\cdot \rightarrow H_2+\cdot X$$

$$HX+RCH_2 \rightarrow RCH_3+\cdot X$$

Under the dilution effect of the HX and the active substances as -OH, -O, the concentration of aboved free radicals can be reduced, which will slow down or suspend the chain reaction of combustion, and achieved the goal of flame resistance.

(b) The tiny particles can be produced to combine with free radicals and terminate the chain reaction or combustion reaction when the flame retardant decomposed.

(c) Large amount of inert gases can be produced when the flame retardants were decomposed at higher temperature, the inert gases can dilute the oxgen concentration in air and the gas state combustible intermediates, further decrease the temperature of combustible gases, and suspend the combustion.

(d) The high density steam can be generated when the flame retardants were heated, and the steam can cover the combutible gases, isolate the combustible gases and oxgen in air, so the combustion can be terminated.

(2) Mechanism of condensed phase flame resistance

The combustion was prevented by delaying or suspending the decomposition reactions of combustible gases in the condensed phase, some circumstances were included as following:

(a) The thermal decomposition of polymers can be retarded or prevented in the solid phase, the decomposed combustible gases and radicals of maintaining chain reaction can be produced by the aboved thermal decomposition.

(b) Lots of inorganic fillers were put into the flame retarded solid substances, the fillers have higher thermal capacity, they can store heat and conduct heat, therefore, the thermal decomposition temperature can be reached.

(c) The flame retardants decomposed and adsorbed heat, prevented the temperature rising, such as, $Al(OH)_3$ and $Mg(OH)_2$.

(d) The porous char layers can be formed on the surface of combusted flame retarted polymers, the char layers can isolute the heat and oxgen, and prevent the combustible gases into the combustion gases, suspend the whole combustion. The phosphorous containning and intumescent flame retardants were belonged to this mechanism.

(3) Mechanism of interrupting heat exchange

The partial heat produced by polymer combustion were taken away, and the absorbed heat were reduced, resulting the thermal decompostion temperature of polymer can be reached, and the combutible gases maintained the whole combustion can be provided continuously, the combustion was self-extinguished.

The combustion and flame retardance are very complicated processes, which involve plenty of influence and restraint factors. It is really hard to distinguish the specific flame retardance mechanism of each flame retardant, in fact, some combination flame retardance mechanisms are taken place at the same time for many flame retardants.

1.5 Research progress of flame retarded epoxy resin

Halogen-free flame retarded epoxy resins were prepared by adding additive halogen free flame retardants or reactive flame retardants to improve the flame retardance of epoxy resin. In recent years, much more reports were published to prepare novel high performance epoxy resin by putting halogen free flame retarded functional groups, functional modification or designing and synthesizing flame retardance curing agents into epoxy resin [15-20]. The recent research progress about halogen free flame retarded epoxy resin will be listed in the following part.

Gu et al. [21] synthesized two novel phosphorous-nitrogen containning flame retardants DP-DDE and DP-DDS for preparing flame retarded epoxy resin, the specific structures were given in Fig.1.2. The results showed that the flame retardance reached UL 94 V-0 rating when the phosphorous content was 0.75%, the residual char was more

than 22% at 800℃, and the heat resistance was also perfect, the Tg was higher thant 135℃, the flame retarded composites had an excellent combination performance.

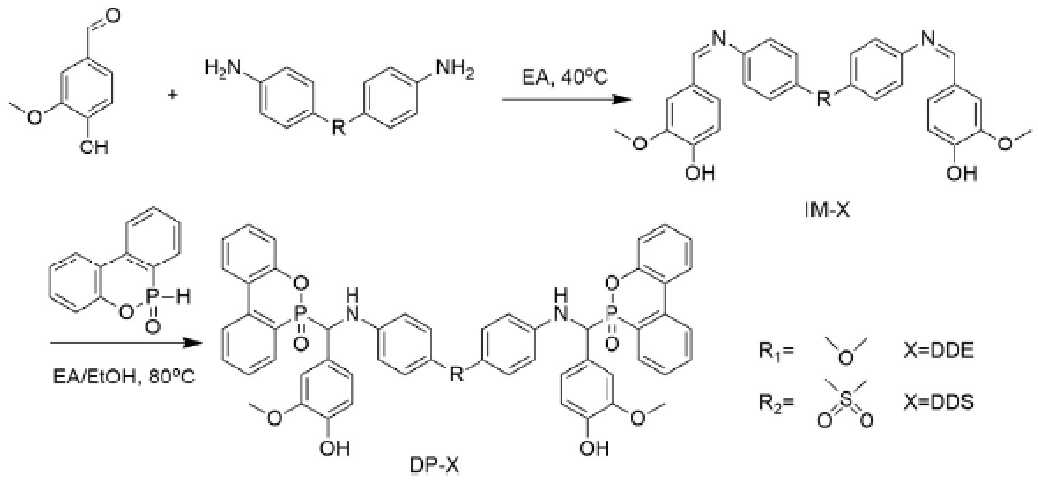


Fig.1.2 The structures of DP-DDE and DP-DDS

Liu et al. [22] synthesized flame retarded epoxy resin by using pohosphonitrilic chloride trimer, phenol, 4-methoxyphenol and epoxy chloropropane, and the specific structure was shown in Fig.1.3. The flame retardance of curing composite was prepared by selecting methyl tetrahydrophthalic anhydride, 4,4-diamino diphenylmethane and linear phenolic resin as the curing agents, and the results showed that the Tg of cured composite was higher than 150℃, the residual char was more than 40% at 750℃ in air, the LOI was more than 30 and reached UL 94 V-0, the composite had good combination performance and a promising potential application.

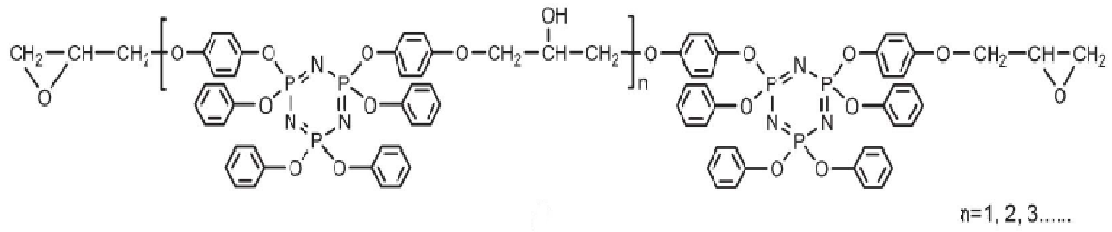


Fig.1.3 The structure of flame retarded epoxy resin

Sara Jirasutsakul et al. [23] synthesized two amine type flame retardant and curing agent of PPEDD and PPPDD for preparing cured flame retarded epoxy resin, the results proved that the LOI values of epoxy composites cured by PPEDD and PPPDD improved from 20 (cured by EDA) and 21(cured by PDA) to 27 and 31 respectively. Xiong YQ et al. [24] synthesized hydroxyl containning flame retardant and curing agent by using melamine, p-hydroxy benzaldehyde and DOPO, and its structure was shown in Fig.1.4. The results showed that the prepared curing agent had excellent thermal resistance and flame resistance, the Tg was 165.5℃, initial decomposition temperature was 321℃, the residual char was 27% at 800℃, and the LOI was 35, the curing agent was especially for preparing flame retarded epoxy resin.

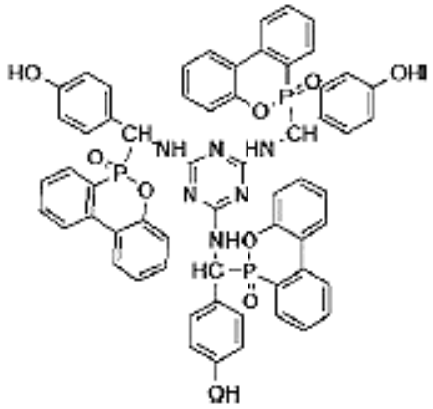


Fig.1.4 The structure of P-MSB

Krishnamoorthy K et al. [25] synthesized a kind of polyamine phosphorous containning flame retardant and curing agent (ATCP, as shown in Fig.1.5) by using phospho-triclic chloride trimer and 4-acetaminophenol. The research found that the initial decomposition temperature in air was 334℃, the residual char was 41.2% at 800℃, when the ATCP content was 15%, and coordinated with ERHA and Bz-EP. Compared with pure Bz-EP, the LOI improved from 28 to 51, and passed the UL 94 V-0, the results from cone calorimeter showed that the PHRR and THR decreased from 713kw/m^2 and 64MJ/m^2 to 289kw/$m^2$and 31 MJ/m^2 respectively, which exhibited good thermal resistance and flame retardance.

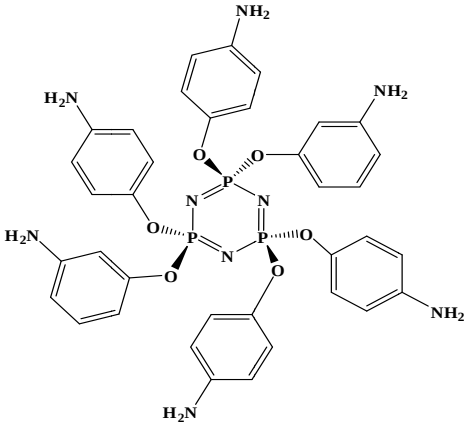


Fig.1.5 The structure of ATCP

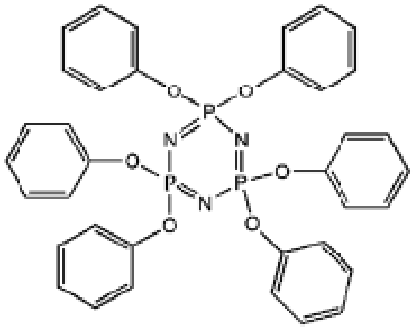


Fig.1.6 The structure of HPCTP

Zhang CL [26] et al. synthesized phosphorous nitrogen intumescent flame retardant HPCTP (shown in Fig.1.6) by using phosphonitrilic chloride trimer and phenol, filled the flame retardant into epoxy resin to prepare halogen free flame retarded epoxy resin composite. The Tg of system containning 2% phosphorous was 190, initial decomposition temperature was 320℃, the residual char was 10.5% at 700℃. The results from cone calorimeter showed that the PHRR and THR decreased from 1034 kw/m^2 and 114 MJ/m^2 to 785 kw/m^2 and 81 MJ/m^2 respectively, and the LOI was 28.6,

passed UL 94 V-0 rating, which exhibited good combination performance. Lv et al. [27] synthesized a kind of oligomer flame retardant PMPC (shown in Fig.1.7) using melamine, $POCl_3$ and ethyl carbamate. The results showed that the composite was filled with 25% PMPC, the initial decomposition temperature was 288, the residual char was 11.4% at 800, the PHRR and THR decreased from 781 kw/m^2 and 76 MJ/m^2 to 292 kw/m^2 and 30 MJ/m^2 respectively, and the LOI was 28, passed UL 94 V-0 rating.

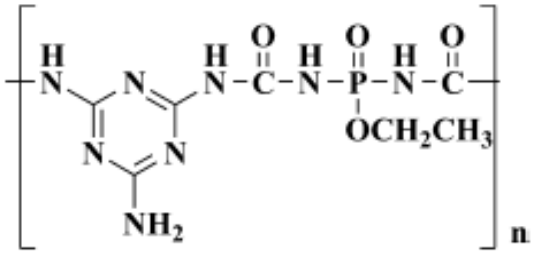


Fig.1.7 The structure of PMPC

Jiao et al. [28] prepared phosphorous containning epoxy resin (FREP) by the reaction between phosphoric acid and bisphenol A epoxy resin (BAEP), the structure was shown in Fig.1.8. The T31 was used as curing agent, and triphenylphosphine was accelerator, BAEP and FREP were utilized to prepare flame retarded composite. The results showed that the LOI of flame retarded composite with the FREP content of 75% was 31.5, and reached UL 94 V-0 rating, exhibited better flame resistance.

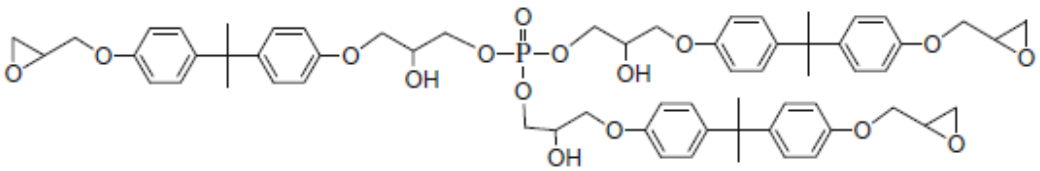


Fig.1.8 The structure of phosphorous containning epoxy resin (FREP)

Raphael Menardab et al. [29] synthesized reactive epoxy resin flame retardant by using m-trihydroxybenzene, epoxy chloropropane and phosphite. The Tg values of

composites with curing agents of IPDA, DA10 and DIFFA were 139℃, 155℃ and 87℃ when the phosphorous content was 3%. The PHRR and THR of pure epoxy resin were 664 kw/m^2 and 34.2 MJ/m^2, after the filling of phosphorous containning epoxy resin P2EP1P, the PHRR and THR of composite reduced to 145 kw/m^2 and 18.2 MJ/m^2. Wang X et al. [30] prepared PPA-g-GNS by grafting a kind of polyphosphamide (PPA) onto the graphene nanosheets (GNS), and the structure of PPA was shown in Fig. 1.9. The PPA-g-GNS was put into the epoxy resin to prepare epoxy resin/PPA-g-GNS composite. The results showed that the LOI of flame retarded epoxy resin increased from 21.5 to 30.5, the PHRR and THR decreased from 1730 kw/m^2 and 113 MJ/m^2 to 1016 kw/m^2 and 569 MJ/m^2 respectively, when the content of PPA-g-GNS was 8% in the composite, the composite had an excellent flame resistance.

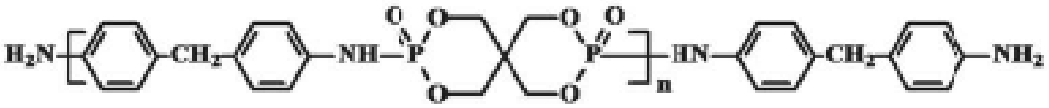


Fig.1.9 The structure of PPA

Yu B et al. [31] prepared phosphorous-nitrogen wrapped modified reduced graphene oxide (FRGO) by one-step method through covalent linkage to epoxy resin, and prepared flame retarded nanocomposite. The results showed that when the content of FRGO was 4 wt%, the composite had better flame retardance, and the THR reduced by 30.2%, PHRR reduced by 43.0%, the LOI increased from 22 to 24.5. Wang R et al. [32] wrapped the graphene oxide by sol-gel and surface treatment method with incombustible silica, and put it into epoxy resin. The results showed that the PHRR and THR decreased by 39% and 10% respectively, the LOI value was the 1.11 times of pure epoxy resin, when the content of functionalized graphene oxide was 1.5%. Wang Z H et

al. [33] synthesized P, Si containning grafting modified graphene (shown in Fig.1.10) by using 3-aminopropyl triethoxysilicane, phenyl dichloro sphosphineoxide and graphene oxide, the functionalized graphene was put into epoxy rsin and the flame retardance of composite was studied in detail. The results showed that the PHRR reduced by 44.7%, THR reduced by 43%, and the LOI increased from 20 to 24, when the content of functionalized graphene was 1%.

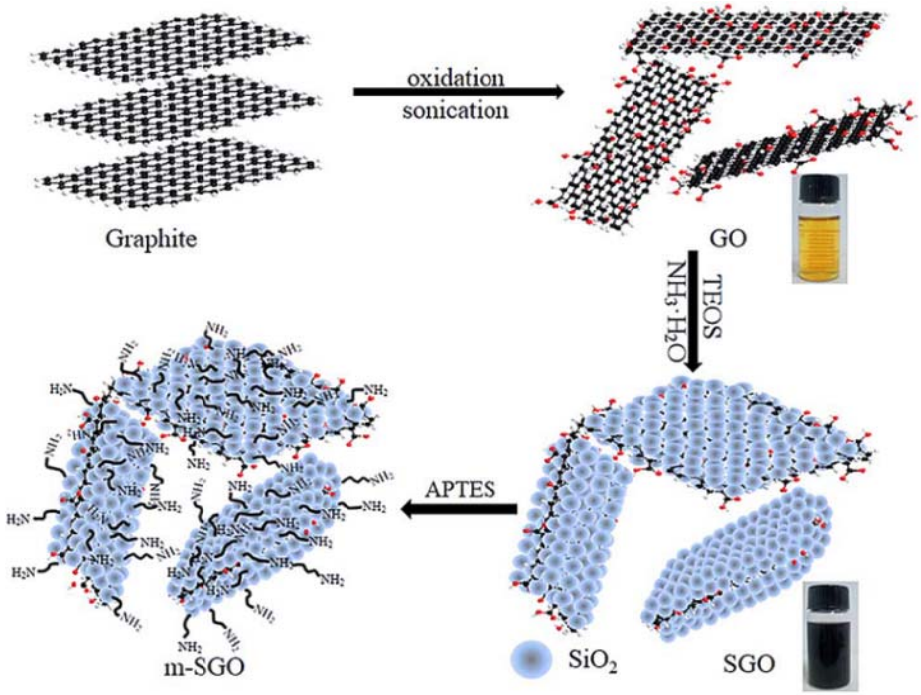


Fig.1.10 The grafting modified graphene by P and Si elements

Qian L J et al. [34] prepared a series of halogen free flame retarded epoxy resin composite by using DOPO derivative (TGIC-DOPO, in Fig.1.11) as flame retardant, DDM, DDS and m-PDA as different curing agents. The results showed that the composite cured by DDM had better flame resistance, when the content of TGIC-DOPO was 4%, the LOI was 35.6 and passed UL 94 V-0 rating, that was a better halogen free flame retarded composite system. Liao SH et al. [35] prepared DOPO-rGO by grafting DOPO onto the graphene oxide, the structure was shown in Fig.1.12. The flame

resistance was studied in detail, and the results showed that the intial decomposition temperature of composite was 340℃, the residual char was 26% at 800℃, the LOI increased to 26 from 20, when the content of DOPO-rGO was 10 wt%. The composite had better thermal stability, and the DOPO-rGO had great effect on the production of char.

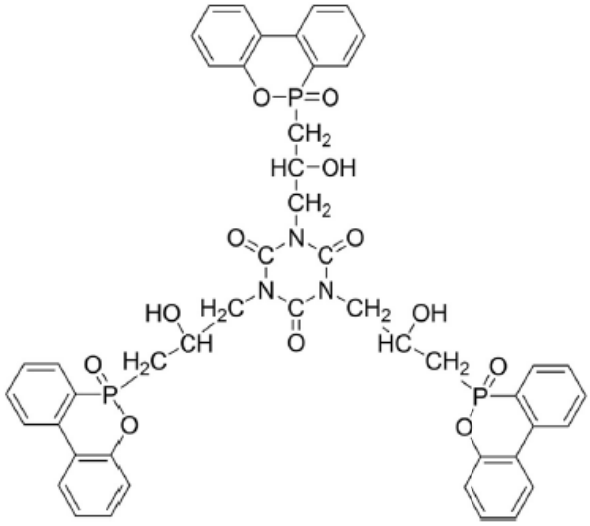


Fig.1.11 The structure of DOPO derivative TGIC-DOPO

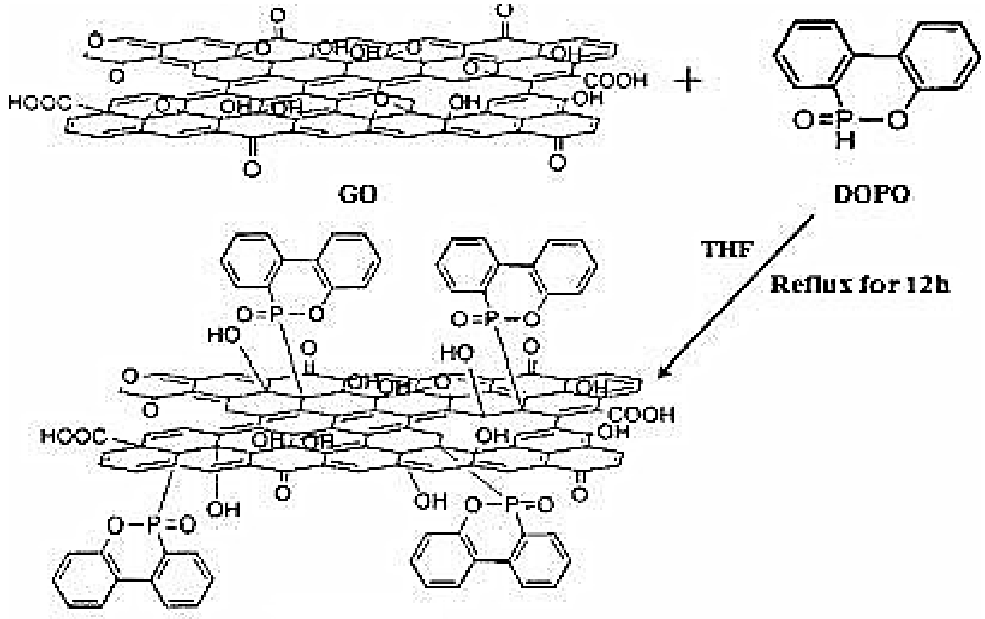


Fig.1.12 The structure of DOPO-rGO

Liu SM [36] et al. synthesized P, N and P containing synergistic compound flame retardant PBN by using DOPO formaldehyde derivative and tributyl borate as shown in Fig. 1.13, the PBN was put into the EP resin, when the content of P and N in the composite was 1.43 amd 0.4, the initial decomposition temperature was 350.5℃, and the maximum decomposition temperature was 416℃, the residual char at 800℃ was 18.2%. The LOI value of flame retarded composite was 34.3, reached UL 94 V-0 rating, the composite had better synergistic flame resistance and combination performance.

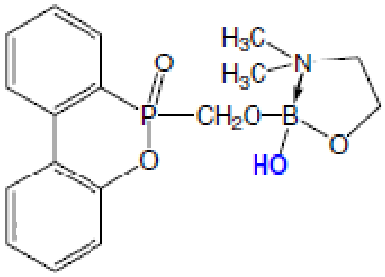


Fig. 1.13 The structure of PBN

Zhao W [37] et al. synthesized polymerization phosphate flame retardant PBDP based on the phenol, $POCl_3$ and bisphenol A. The results show that when the loading fraction of PBDP in epoxy resin was 20%, the PHRR and THR decreased to 474 kw/m^2 and 30.6 MJ/m^2 respectively from 928 kw/m^2 and 39 MJ/m^2, and the LOI was 29.8, reached UL 94 V-0 rating. Carja ID et al [38] synthesized flame retardant PFR for EP as shown in Fig. 1.14 based on DOPO derivative and DCPPO. The results show that the LOI was 40.5 when the phosphorous fraction in the system was 2%, and reached UL-94 V-0 rating, the PHRR and THR decreased to 164.4 kw/m^2 and 57.4 MJ/m^2 respectively from 275.5 kw/m^2 and 56.8 MJ/m^2.

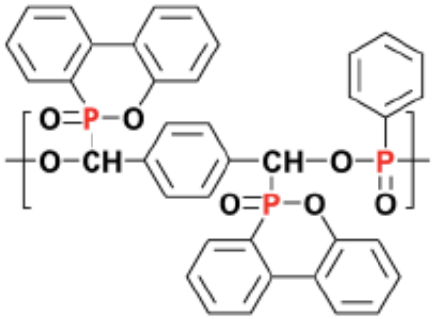


Fig. 1.14 The structure of flame retardant PFR

Xu JZ et al. [39] successfully synthesized polyhydroxyl epoxy resin flame retardant & curing agent HHPCP with phosphonitrilic chloride trimer and p-hydroxy benzaldehyde as shown in Fig. 1.15. When the loading fraction of HHPCP in composite was 10%, the flame retarded EP composite was 26.5, and reached UL 94 V-0 rating. The residual char was 15.5% at 900℃, the composite had a better flame resistance and heat resistance.

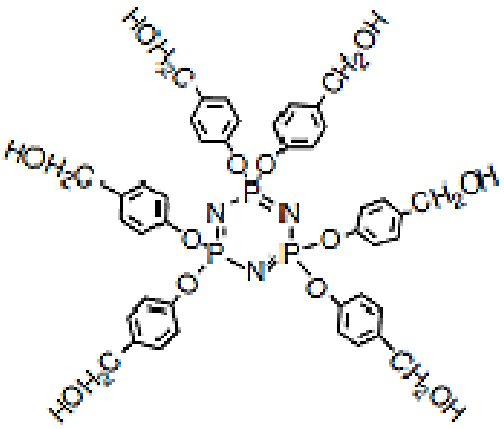


Fig. 1.15 The structure of flame retardant HHPCP

Tian NN et al. [40] synthesized a polymerization type flame retardant PCPBO with $POCl_3$, pentaerythritol and bisphenol A as provided in Fig.1.16. When the loading content of PCPBO in whole system was 20%, the initial decomposition temperature of

composite in nitrogen was 267℃, the residual char was 16.6%, the PHRR and THR decreased to 337.1 kw/m^2 and 117.3 MJ/m^2 respectively from 1160.9 kw/m^2 and 135 MJ/m^2, and the LOI was 31.2, reached UL 94 V-0 rating.

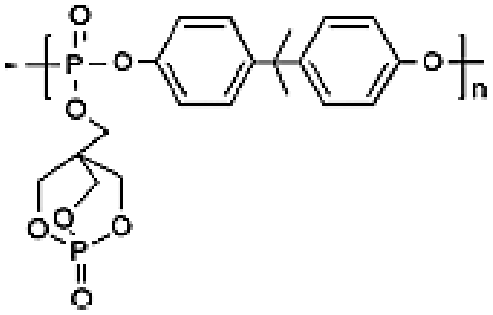


Fig. 1.16 The structure of PCPBO

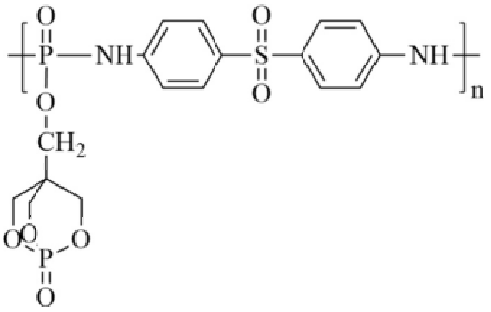


Fig. 1.17 The structure of PSA

Zhao W et al. [41] synthesized a polymerization type flame retardant PSA for epoxy resin with $POCl_3$, pentaerythritol and 4,4-diaminodiphenyl sulphone as shown in Fig.1.17. When the loading content of PSA in whole system was 20%, the initial decomposition temperature of composite in air was 313℃, the residual char was 22.6% at 700℃, the PHRR and THR decreased to 118 kw/m^2 and 21.7 MJ/m^2 respectively from 469 kw/m^2 and 66.2 MJ/m^2, and the LOI was 31.0, reached UL 94 V-0 rating. The flame retarded composite showed excellent flame resistance and heat resistance, PSA had a promising application potential in the field of flame retardant.

You GY et al. [42] synthesized a novel P and N containing intumescent flame retardant polymerization type flame retardant NDP for epoxy resin as shown in Fig.1.18. When the phosphorous content in whole system was 1.5%, the initial decomposition temperature of composite in nitrogen was 237.6℃, the residual char was 30.8% at 800℃, and the LOI was 31.0, reached UL 94 V-0 rating. The flame retarded composite showed excellent flame resistance.

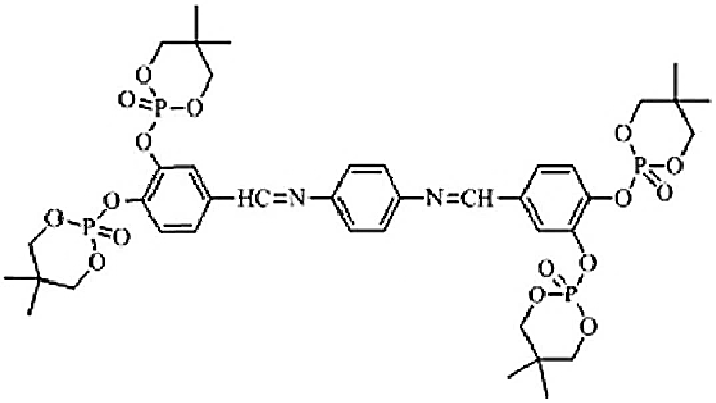


Fig. 1.18 The structure of NDP

Sun J et al. [43] synthesized a novel epoxy resin containing flame retardant groups with phosphonitrilic chloride trimer, ethylenediamine, phenol, bisphenol A and epoxy chloropropane as shown in Fig.1.19. The resin was cured by DDM, DDS and linear phenolic aldehyde resin, respectively, the values of Tg was 157, 159 and 164℃, the initial decomposition temperature of composite in nitrogen was 287, 315 and 286℃, and the residual char was 31.01, 38.48 and 36.3% at 750℃ respectively, and the values of LOI was 31.12, 32.54 and 30.76, all the samples reached UL 94 V-0 rating.

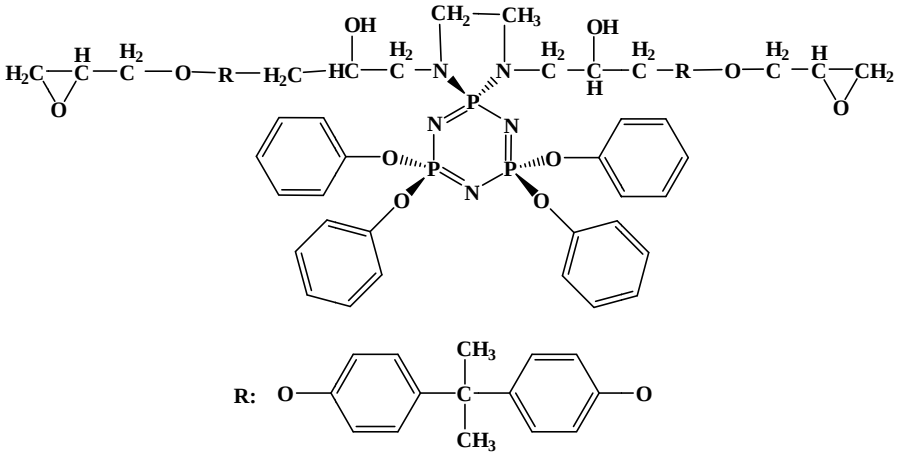


Fig. 1.19 The structure of epoxy resin containing flame retardant groups

Liu H et al. [44] synthesized a novel flame retarded epoxy resin PN-EPC with phosphonitrilic chloride trimer, phenol, bisphenol A and epoxy chloropropane as shown

in Fig.1.20. The resin was consisted of PN-EPC and DGEBA. When the PN-EPC content in whole system was 20%, the resin was cured by DICY, DDM and MeTHPA, respectively, the values of Tg was 143, 148 and 123℃, the initial decomposition temperature of composite in nitrogen was 262, 285 and 266℃, and the residual char was 32.12, 25.75 and 22.71% at 750℃ respectively, and the values of LOI was 31.8, 31.2 and 30.2, all the samples reached UL 94 V-0 rating.

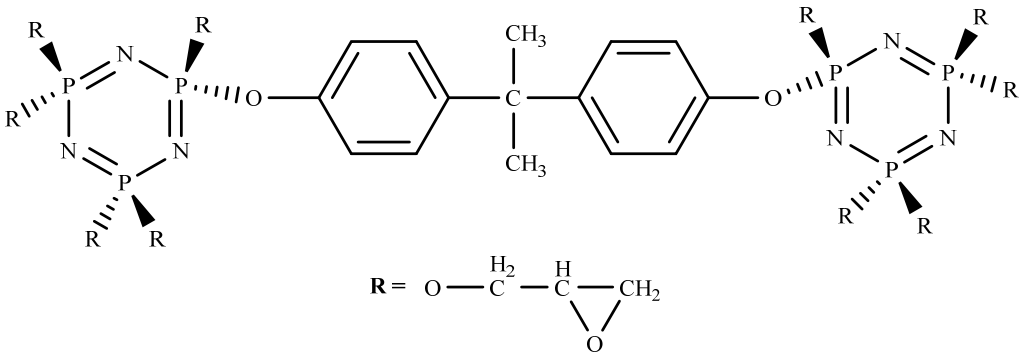


Fig. 1.20 The structure of PN-EPC

Bai YW et al. [45] synthesized a novel halogen-free flame retarded epoxy resin with phosphonitrilic chloride trimer, bisphenol A and glycidol as shown in Fig.1.21. The resin was cured by DDM, DDS and linear, respectively, the values of Tg was 157, 159 and 164℃, the initial decomposition temperature of composite in nitrogen was 287, 315 and 286℃, and the residual char was 26.68, 33.24 and 37.72% at 750℃ respectively, and the values of LOI was 32.4, 31.6 and 30.2 respectively, all the samples had excellent flame resistance.

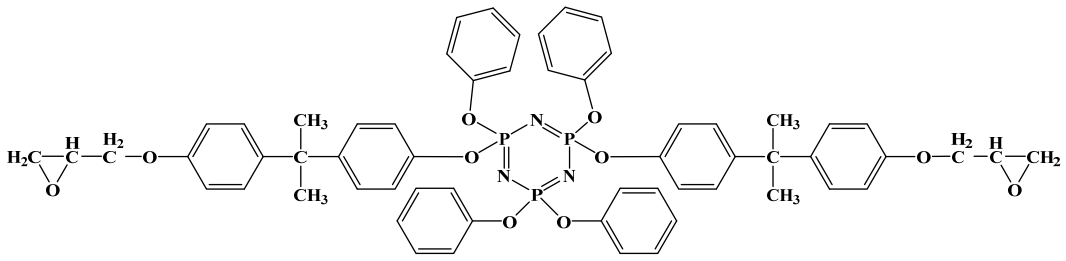


Fig. 1.21 The structure of flame retarded epoxy resin

1.6 Purpose and contents of the present study

Because of the easy-burning disadvantages of epoxy resins, some novel flame retardants or compound flame retardants were attempted to be synthesized or prepared to enhance the flame resistance and mechanical performance of flame retarded epoxy resin composites. The whole paper can be devided into 6 parts as follows:

In the second chapter, the compound flame retardants consisting of MH/ATH/MRP were prepared successfully. The MRP was synthesized through in-situ polymerization method by wrapping melamine-formaldehyde resin on the red phosphrous particles. The best ratio of compound flame retardants of MH/ATH/RP was testified as 46/46/8, when filling with 45 wt% compound flame retardants, the prepared PE composite had a better combination properties, tensile strength was 10.3 MPa, impact strength was 13.5 kJ/m^2, the LOI was 29.1%, vertical burning reached UL 94 V-1 rating. In order to improve the mechanical properties further, two polymeric compatibilizers POE-g-MAH and EPDM-g-MAH were used to toughen the composite.

In the third chapter, a novel phosphorous-containning hardener and flame retardant, aryl phosphinate dianhydride BPAODOPE was synthesized successfully, and used for preparing halogen-free flameretarded epoxy resins when coupled with another curing agent. The epoxy resin composites filling with BPAODOPE had excellent flame resistance and higher char yield, and the flame resistance and char yields of the flame retarded epoxy resins increased with an increase of phosphorus content, and the heat resistance and mechanical performance were studied in detail.

In the fourth chapter, another novel phosphorus containning flame retardant and curing agent PES was synthesized successfully with pentaerythritol, phosphorus oxychloride and ethylenediamine, the structure and performance of production was

characterized in detail. The synthesized PES and DDS was used as flame retardant and curing agent, and the flame retarded epoxy resin composites were prepared with different phosphorus content. The heat resistance, flame retardance, microstructure and mechanical performance of flame retarded epoxy resin composites were researched in detail with the synthesized phosphorus containning PES.

In the fifth chapter, the intumescent flame retardant containing phosphorus and nitrogen PDEPDM was prepared successfully by three step reactions, and the suitable reaction conditions were tested under different reaction temperature, reaction time and solvent ratio. As-synthesized PDEPDM was charactered by the FTIR, NMR and TG. The application of PDEPDM in polyethylene was attempted, relative performance of the flame resistance, heat resistance, microstructure and mechanical performance were researched in detail.

In the sixth chapter, a novel P and N containing compound PMXSPB was synthesized and used as a flame-retardant and curing agent to prepare flameretarded EP resin composites. The EP resin composites filled with PMXSPB exhibited excellent flame resistance and mechanical properties. The flame resistance and char yields of flame-retarded EP resins increased with increasing PMXSPB content. Compared with BPAODOPE, phosphorus containing flame-retardant and curing agents synthesized in Charpter 3, PMXSPB has a higher phosphorus fraction per unit mass, a lower fraction of assistant curing agent, and much higher flame resistance efficiency.

In the seventh chapter, novel flame retardant (PPSDB) containing phosphorus, nitrogen and boron was synthesized and its chemical structure was confirmed by FTIR and ^{1}HNMR. The thermal stability of PPSDB was confirmed to meet the requirement for fabricating PE composites by TGA. PE/PPSDB composites showed good flame

resistance, antidripping properties and compatibility. When the PPSDB fraction was 30 wt% in the PE/PPSDB composite, the LOI value was 29.2, vertical burning reached UL-94 V-0 rating, and the tensile strength and notched impact strength were 18.6 MPa and 12.5 kJ/m^2, respectively. The PPSDB integrated the P, N and B elements by forming the non-polar phenyl and spirocyclic groups, which has a positive effect in improving the flame resistance efficiency and the compatibility between the flame retardant and PE matrix.

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Chapter 2

Preparation of microencapsulated red phosphorous flame retardant and its application in polyethylene

2.1 Introduction

Polyethylene (PE) is a large-consumed polymer employed in many applications, but as well known one of its most disadvantages is its combustion when applying in electronic and electrical productions. Common method to obtain flame retarded PE usually requires filling all kinds of flame retardants. In recent years, developing non-halogen flame retarded PE materials with low emission of smoke and poisonous gases has become a potential trend [1-3]. Many investigations have demonstrated that magnesium hydroxide (MH) and aluminium hydroxide (ATH) are the most widely used non-toxic and smoke suppressing flame retardant additives. However, more than 60% loading of MH or ATH is required to achieve the flame resistance. Numerous investigations have been made on the flame retardant synergistic agents of MH or ATH [4-6] to improve their flame retardant efficiency. In composites, nonpolar polyolefins are incompatible with the conventional hydrophilic fillers, it is difficult to obtain good dispersion when polymers filling with various polar inorganic particles. Thus, adhesion is poor between the filler surfaces and polymer matrix. However, the filler surfaces can be modified by using different coupling agents [7], such as organosilanes, fatty acids and their salts, to improve the interfacial adhesion at the boundary between the filler and polymer matrix. The microencapsulation technique is another good choice. Melamine-formaldehyde (MF) and urea-formaldehyde (UF) resins are commonly used as shell materials in the microencapsulation, for example, Wuet al. [8, 9] prepared

microcapsulated red phosphorus and studied its flame retardant mechanism in halogen-free flame retardant polyolefins, and also prepared microencapsulated ammonium polyphosphate with urea-melamine-formaldehyde shell. Furthermore, polymeric compatibilizer can be applied in polyolefin-based composites to improve the adhesion between filler particles and matrix resins [10]. Grafting polyolefin polymers containing carbonyl group werewidely used to increase the polarity of the polymers. Reactive groups interacted with functional groups on the inorganic filler, and long hydrocarbon tails were able to anchor to the polymer matrix through physical entanglements and Vander Waals interactions [11]. Many kinds of polymeric compatibilizers had been used to toughen the composites [12-16], including acrylic acid functionalized polypropylene (PP-g-AA), maleic anhydride functionalized polyolefin (PE-g-MAH), polypropylene (PP-g-MAH), ethylene-propylene rubber (EPR-g-MAH) and dibutyl maleate (DBM) functionalized polyolefin (PE-g-DBM), while POE-g-MAH and EPDM-g-MAH were seldom reported as compatibilizers filling in PE composites.

Herein microencapsulated red phosphorous (MRP) was synthesized and used as the synergistic agent for MH and ATH compound flame retardants. Meanwhile, base on the best proportion of three flame retardants, POE-g-MAH and EPDM-g-MAH compatibilizers were selected to toughen flame retarded PE composites. Finally, flame retarded PE composite with better combination performance was prepared, and the mechanisms of flame retardance and toughning were also studied in detail.

2.2 Experiment

2.2.1 Materials

Low density polyethylene (PE), coded as 18D was purchased from Daqing

petrochemical corporation of PetroChina; EPDM-g-MAH and POE-g-MAH were obtained from Shenyang Siwei polymer corporation; magnesium hydroxide (MH, 10μm)and aluminium hydroxide (ATH,15 μm) were supplied by Haicheng Jinghua micro-powder factory and Aluminum Corporation of China, respectively; red phosphorous (RP), melamine, formaldehyde, sodium hydroxide, phosphoric acid were all analytical gradeand purchased from Shanghai Sinopharm Chemical Reagent Company.

2.2.2 Preparation of microencapsulated red phosphorous (MRP)

4.5 g of melamine, 4.0 g of formaldehyde, and 40ml of distilled water were put into a three-neck flask. The pH value of the suspension was adjusted to 7.5 with sodium hydroxide and then the reaction mixture was heated to 70^{o}C. The suspension liquid was kept for 30 min at the same temperature after it became transparent by cooling to room temperature the oligomer solution of melamine-formaldehyde was synthesized. The second step to prepare the MRP sample was described as following: 40 g of red phosphorus powder and 100 ml of distilled water was added into the above oligomer solution. The pH value of the mixture was adjusted to 4.5-5.0 with aqueous phosphoric acid. The mixture was stirred for 30 min and heated to 80^{o}C for 50 min. The reaction mixtureswere kept for another 1 h at the same temperature, and then cool to room temperature. The reaction mixture was filtered, and the solid so obtained was washed three times with distilled water, and dried in an oven at 80^{o}C to obtainthe target MRP powder sample.

2.2.3 Preparation of flame retarded PE samples

Blended the flame retardants with PE and commercial compatibilizers in a high speed mixer, then the blends were extruded in melt state by using a corotating twin-screw extruder (TSE-35A, the screw diameter is 35.6mm, screw speed is 600 rpm, and the output rate is 45 kg/h, Nanjing Ruiya Polymer Processing Equipment Corporation) at 200-220^{o}C, the extrudate was granulated to produce small granules of flame retarded PE, in addition, these granules were dried for 5 h at 80 ^{o}C before the specimenswere prepared. The final standard samples were injected by injection molding machine (NG-120A, Wuxi Grand Tech Machinery Co. Ltd.).

2.2.4 Analysis and test

X-ray photoelectron spectroscopy (XPS): The XPS spectra was recorded with a VG ESCALAB MK II spectrometer to analyze the components of RP and MRP, using Al kα excitation radiation (hν = 1486.6 eV) in the operation.

Scanning electron microscope (SEM): Morphologies of flame retardant particles and fracture surfaces of samples were observed by field emission scanning electron microscope (JEOL, coded as JSM-6700F, Japan). The specimens were previously coated with a conductive gold layer before SEM scanning.

Limiting oxygen index (LOI): LOI values (the minimum oxygen concentration necessary to ignite the materials) were measured by using a JF-3 type instrument (Nanjing Jiangning Analysis Instrument Factory) on the specimens of 120×6.5×3 mm^3 according to the standard oxygen index test ASTM D 2863-00.

Vertical burning (UL 94 test): UL 94 vertical burning tests were carried out

using a CZF-1 type instrument (Nanjing Jiangning Analysis Instrument Factory) on the sheets of 127×12.7×3 mm^3 according to the standard UL 94 test ASTM D 635-77.

Measurements of mechanical properties: The tensile strength and elongation at break were measured with electric tensile tester (TCS-2000, Taiwan) with a speed of 5mm/min at room temperature. The dumb-bell shaped specimens were prepared according to ASTM D412-87. Charpy impact tests were performed by charpy impact tester (GT-7045-MDL, Taiwan) according to ISO 179-1. In all the mentioned measurements, the listed data was the average values of five samples.

2.3 Results and discussion

2.3.1 Characterization of MRP

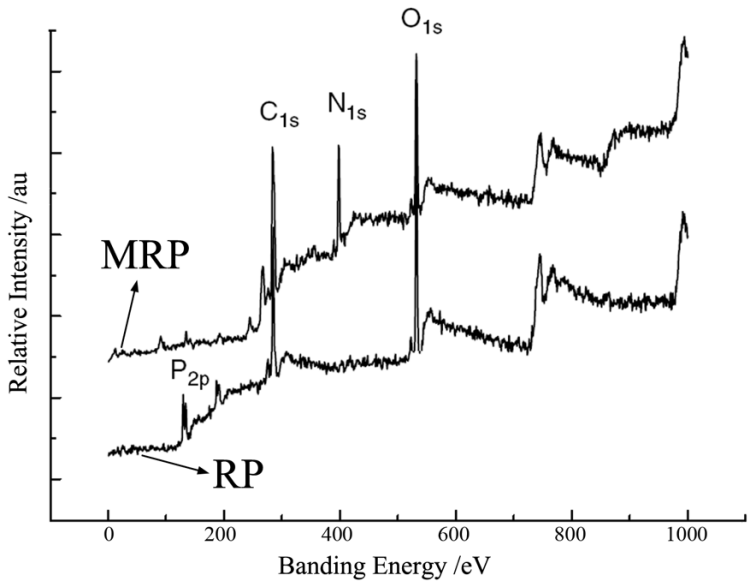

Fig.2.1 XPS spectra of RP and MRP

The XPS spectrum of RP and MRP samples were shown in Fig.2.1, from the spectrum of RP, it can be observed that the peak at 130 eV was assigned to P_{2p} binding energy of phosphorus. Comparing with the peak of RP, MRP spectra also had similar

P_{2p} and O_{1s} peaks, while the P_{2p} peak of phosphorus almost disappeared, and a new peak at 400 eV turned up, whichwas assigned to the N_{1s} binding energy of nitrogen atom that came from the melamine-formaldehyde resin, these results showed that the RP particles had been wrapped by melamine-formaldehyde resin through in-situ polymerization reaction.

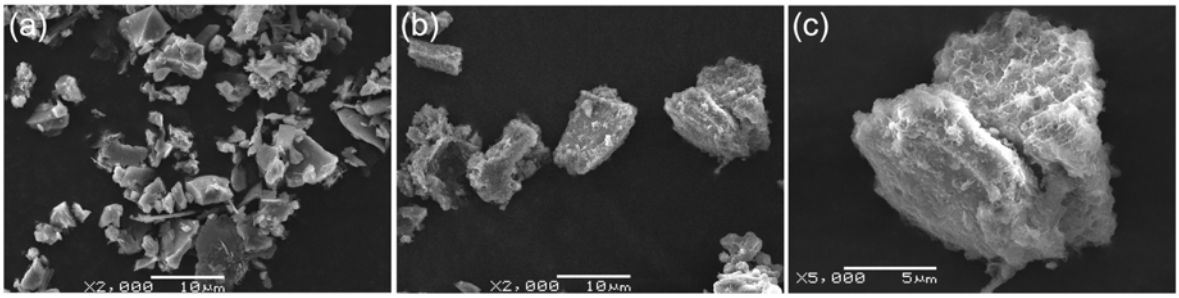

Fig.2.2 Microstructures of RP and MRP particles by SEM, a) RP, b) MRP, c) magnifying particle

The microstructures of RP particles without and with microencapsulation were observed by SEM, as showed in Fig.2.2, the common RP particles were shown in Fig.2.2a, which had poor dispersibility, the particle sizes were irregular, and the particle surfaces were smooth and had obvious edges. While the MRP particles had coarse surfaces just for the melamine-formaldehyde resin cladding, the MRP particles were larger in size, with better dispersive than RP particles, the magnifying right corner particle in Fig.2.2b was just shown in Fig.2.2c, the particle surface was wrapped with netlike substance, which showed that melamine-formaldehyde resin had been wrapped on the surfaces of RP particles, and the flame retardant of MRP had been prepared successfully.

2.3.2 Synergy effect of MRP

In the non-halogen flame retarded PE composite, compound flame retardants consisted of MH, ATH and MRP, the total contents of compound flame retardants were fixedas 45%, the weight ratio of MH and ATH was 1:1, and the weight proportion of MRP was variable. The main reason of 45% total content was just decided by the flame resistance of flame retarded PE composite, the compound flame retardants was consisted of MH, ATH and MRP, which had a poor flame resistance efficiency, if the loading content of compound flame retardants was lower than 45%, the composite couldn't reach the criteria of flame resistance, so the total contents was fixed as 45%.

Table 2.1 Influence of MRP content on the performance of flame retarded PE composites

MH/ATH/MRP	Tensile strength /MPa	Impact strength kJ/m^2	LOI /%	Vertical burning UL 94
50/50/0	9.0	14.3	26.2	V-2
48/48/4	9.7	13.9	27.9	V-2
46/46/8	10.3	13.5	29.1	V-1
44/44/12	10.5	13.4	28.5	V-1
42/42/16	11.9	12.5	27.3	V-2

In order to assess the influence of MRP's content on the performance of composites and obtain the best formula, tensile strength, impact strength, LOI and UL 94 were measured and the performances were listed in Table 2.1. The LOI and vertical burning UL 94 test were widely used to evaluate flame resistance of polymers, especially for selecting flame retardant formula. The LOI and UL 94 rating were listed in Table 2.1, it was found that the flame resistance of PE composites increased at first,

when MRP's content was more than 8 wt%, the flame resistance of the composites gradually declined, the best proportion of MRP was 8 wt%. Compared with the composite filling with MH/ATH, the LOI of composites filling with 8 wt% MRP reached 29.1% from 26.2% and UL 94 rating reached V-l from V-2. The results indicated that the flame resistance of PE composites just improved remarkably by filling MRP and 8 wt% MRP had a better synergistic effect with MH/ATH. The reason of synergistic effect and the best MRP proportion just explained as follows:

As well known, MH and ATH are both inorganic hydroxides, when burning temperature reach 230^{o}C and 340^{o}C, ATH and MH decompose one by one through absorbing heat, the remnants of metal oxide Al_2O_3 and MgO cover the surface of polymers and resist the further burning. MRP plays synergistic effect with MH and ATH, just for red phosphorus (RP) can be predominantly oxidized and adsorb the water which released from MH and ATH, finally form vitreous coverings of various phosphoric acid derivatives, these derivatives can react with resin to form more stable structures containing P-O-P and P-O-C complexes, which promote the formation of compact charred layers in the condensed phase during burning of polymer materials [17]. These compact charred layers prevent the underlying polymer from further attack by heat flux in a flame. Another, the MRP were clad with melamine-formaldehyde resins, the resin shell materials were also improve the flame resistance of PE composites for its flame retardance. When the MRP loading was large enough, the flame resistance of composites would decline just for the combustible RP, and the oxidation of RP is an exothermic reaction, the releasing heat will increase with an increase of RP content, the much heat will be in favor of the combustion of polymer composite.

It can be seen that the MRP content had a certain effect on tensile and impact

strength of composites. There were different trends for the change of tensile strength and impact strength. The tensile strength increased with an increase of MRP content by the large, however, the impact strength of composites gradually decreased when increasing MRP content. Considering the priority of flame resistance of composites, we obtained the best flame retarded PE composite when the proportion of MH/ATH/MRP compound flame retardants was 46/46/8 and the total content was 45%, the LOI was 29.1, vertical burning reached UL 94 V-1 rating, tensile strength and impact strength was 10.3 MPa and 13.5 KJ/m^2 respectively.

2.3.3 Toughening of non-halogen flame retarded PE

Base on the best proportion 46/46/8 of MH/ATH/MRP and the total content was 45%, we put compatibilizers EPDM-g-MAH or POE-g-MAH in PE matrix resin, changed the weight fraction of compatibilizer from 0%, 5%, 10%, 15% to 20% gradually. The samples of flame retarded PE were tested by limit oxygen index (LOI) and vertical burning, the results were shown in Table 2.2.

Table 2.2 Flame resistance of PE composites filling different contents of compatibilizer

Weight fraction of compatibilizers	LOI (%)		Vertical burning (UL 94)	
	EPDM-g-MAH	POE-g-MAH	EPDM-g-MAH	POE-g-MAH
0	29.1	29.1	V-1	V-1
5%	29.3	29.4	V-1	V-0
10%	29.5	30.2	V-0	V-0
15%	30.3	30.7	V-0	V-0
20%	30.8	31.1	V-0	V-0

It can be seen that LOI value increased with an increase of compatibilizer content in all cases. Meanwhile, the levels of vertical burning (UL 94) were also

improved with an increase of compatibilizer content. When the flame retarded composite with no compatibilizer was compared, the LOI of composite increased from 29.1 to 29.5 and vertical burning reached V-0 from V-1 when filling 10 wt% EPDM-g-MAH, under the same condition, the flame retarded PE toughened by POE-g-MAH had a higher LOI value of 30.2%. The results mean that the addition of compatibilizer improved the flame resistance of composites greatly, and the flame resistance contribution of POE-g-MAH was better than EPDM-g-MAH under the same contents from the data in Table 2.2.

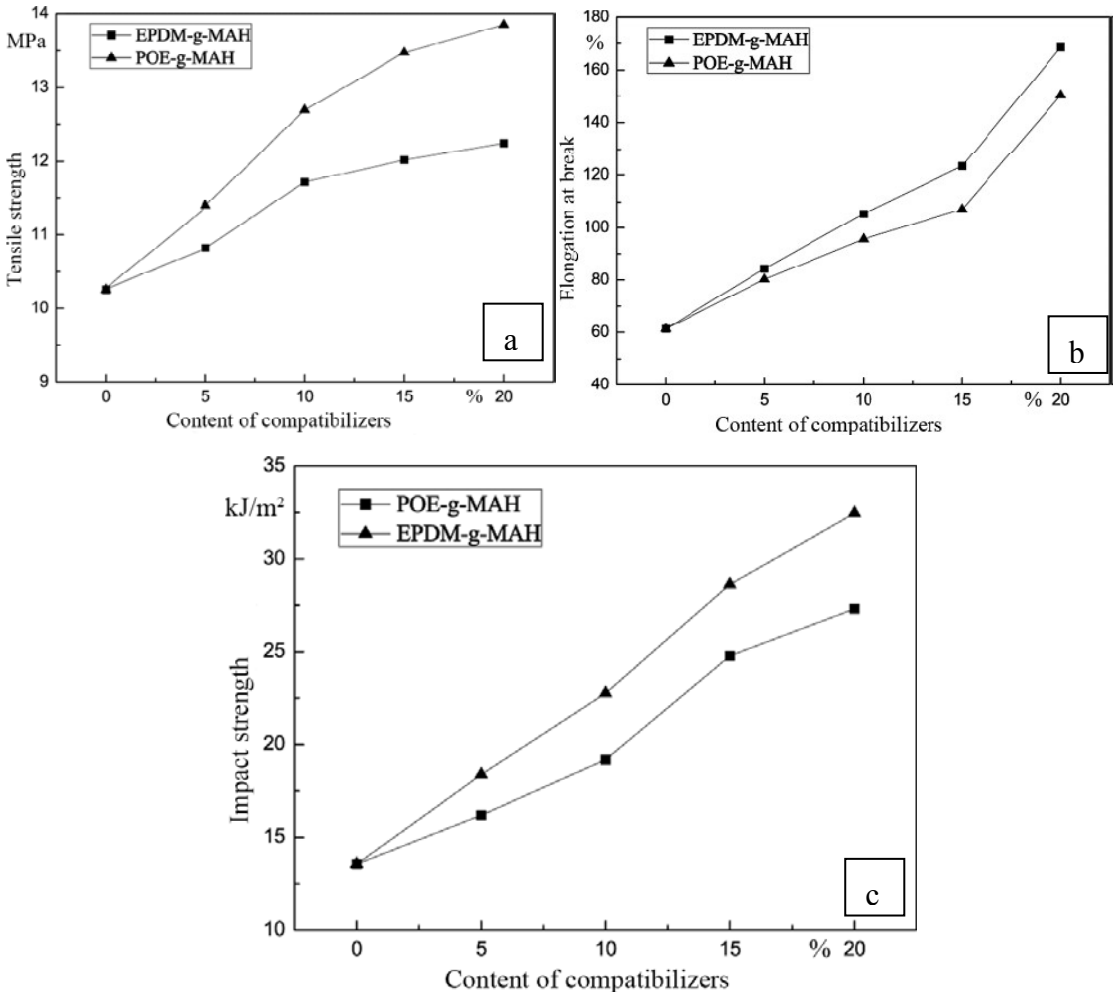

Fig.2.3 Mechanical properties of flame retarded samples with differentcontents of compatibilizer, a) tensile strength, b) elongation at break, c) impact strength

The mechanical properties of the toughened flame retarded PE were characterized by vertical drawing test and charpy impact test, the results were shown in Fig.2.3. Tensile strengthin Fig.2.3a showed an increase tendency with an increase of compatibilizer content. The tensile strength of non-toughened flame retarded PE was 10.3 MPa, while the corresponding values toughened by 20 wt% POE-g-MAH increased to 13.9 MPa, and the sample toughened by 20 wt% EPDM-g-MAH increased to 12.2 MPa, it showed that the composite toughened by POE-g-MAH had higher tensile strength than by EPDM-g-MAH. Toughness of composites can be reflected by elongation at break and impact strength, which was shown in Fig.2.3b and Fig.2.3c, the elongation at break and impact strength also improved significantly with an increase of compatibilizer content, the elongation at break and impact strength of non-toughened flame retarded PE was 61.3% and 13.5 kJ/m^2 respectively, however, the corresponding two data toughened by 20 wt% POE-g-MAH increased to 150.3% and 27.3 kJ/m^2 respectively, the corresponding sample toughened by 20 wt% EPDM-g-MAH increased to 168.6% and 32.5 kJ/m^2, obviously the toughening effect of EPDM-g-MAH was better than POE-g-MAH. These results obviously indicated that both EPDM-g-MAH and POE-g-MAH can be used as an efficient polymeric coupling agent to improve the mechanical properties of composites, while the toughening effect of EPDM-g-MAH was better than POE-g-MAH under the same content. Considering the combination properties of flame retarded PE composite and the cost of polymeric compatibilizers, the flame retarded PE composite filled with 10 wt% EPDM-g-MAH had the best combination performance, the LOI was 29.5, vertical burning reached UL 94 V-0 rating, tensile strength and elongation at break was 11.7 MPa and 105.4% respectively, impact strength was 22.8 kJ/m^2.

The enhancement of mechanical properties of PE composites by filling polymeric compatibilizer could be attributed to the adhesive effect of compatibilizer. A possible reason for improving listed as follows; POE-g-MAH and EPDM-g-MAH were both used as polymeric compatibilizer in the flame retarded PE composite, which containing a certain amount of polar functionality of maleic anhydride (MAH). The polar carboxyl groups (MAH) in the side chains of the grafted EPDM or POE were compatible with inorganic particles, whereas the main chains of the grafted polymer EPDM or POE had good compatibility with PE matrix resin, and thus improve the adhesion [14,16,17] between inorganic particles of flame retardants and PE. The content of MAH functionality decided by the content of compatiblizers, the larger loading of compatibilizers provided much polar MAH which improved the adhesion between inorganic particles and PE, flame retardant particles had better dispersion ability in polymer when there was enough MAH functionality to interact with the hydroxyl groups of the inorganic flame retardants, so the mechanical properties of composites improved greatly with an increase of compatibilizer content.

The addition of polymeric compatibilizers greatly improved the flame resistance of PE composite, a tentative reason was put as follows; the adhesion between inorganic particles of flame retardants and PE resin was improved when filled with much more compatibilizer, and the flame retardant particles had distributed uniformly in the PE matrix, the uniform distribution of inorganic flame retardant particles was just the reason for the improvement of flame resistance.

2.3.4 Microstructure analysis on the surface of fracture

In order to further testify the compatibilization effect of polymeric

compatibilizer, the morphologies of the fractured surface of flame retarded samples were characterized by SEM and shown in Fig.2.4. The morphology of the fracture surface of non-toughened samples was shown in Fig.2.4 a, it can be seen clearly that many inorganic particles on the fracture surface, which showed that the dispersion of particles in the polymer matrix is not good, meanwhile the macroscopic fractured surface was smooth and had a brittle nature, thus the composite exhibited low impact strength. Fig.2.4 b and c showed the fracture surfaces of PE composites toughening by 20 wt% POE-g-MAH and 20 wt% EPDM-g-MAH compatibilizer, which was observed that no clear interface existing between inorganic particles and PE matrix, and flame retardant particles were well dispersed into the polymeric matrix. This means that the adhesion between inorganic particles and PE matrix increased when filling with the grafted polymer compatibilizer. Comparing to flame retarded PE composite toughening by POE-g-MAH in Fig.2.4 b, the fractured surface of the composite by EPDM-g-MAH became rough banding shape in Fig.2.4 c, the banding shape of EPDM will bridge across the propagating cracks when the crack-opening process, the bridging effect of banding EPDM fibers was beneficial for improving the fracture toughness of the composite, which further testified the toughening effect of EPDM-g-MAH was better than POE-g-MAH under the same circumstance.

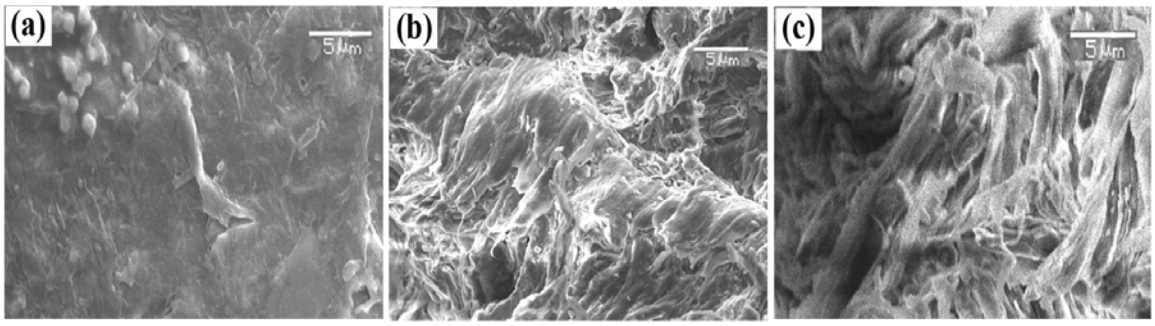

Fig.2.4 Fractured surfaces of samples, a) common, b) 20 wt% POE-g-MAH, c) 20 wt%

EPDM-g-MAH

2.4 Conclusions

In this chapter, flame retarded PE composites were prepared successfully with MH/ATH/MRP compound flame retardants. Firstly, MRP was synthesized through in-situ polymerization method and characterized by XPS and SEM, it was used as a synergistic agent for MH and ATH. The best ratio of compound flame retardants of MH/ATH/RP was testified as 46/46/8, when filling with 45 wt% compound flame retardants as above ratio, the prepared PE composite had a better combination properties, tensile strength was 10.3 MPa, impact strength was 13.5 kJ/m^2, the LOI was 29.1, vertical burning reached UL 94 V-1 rating. In order to improve the mechanical properties further, two polymeric compatibilizers POE-g-MAH and EPDM-g-MAH were used to toughen the composite. The results showed that the addition of compatibilizer improved the flame resistance and mechanical properties of composite greatly. POE-g-MAH had higher contribution in flame resistance, and EPDM-g-MAH had a better toughening effect under the same circumstance. Considering the cost/performance ratio, the flame retarded PE composite filling with 10 wt% EPDM-g-MAH had the best performance, LOI was 29.5, vertical burning reached UL 94 V-0 rating, tensile strength and elongation at break were 11.7 MPa and 105.4%, impact strength was 22.8 kJ/m^2. The recipe of flame retarded PE composite can be applied in non-halogen flame retarded cables or other relative products.

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Chapter 3

Synthesis of a novel curing agent BPAODOPE and its application in epoxy resin

3.1 Introduction

Epoxy resins are widely used in the fields of electronic/electrical industry and transportation because of their excellent electrical and mechanical properties [1]. However, the flammability of the resin is a major limitation in the application of requiring high heat resistance and flame resistance. Generally, halogen flame retardants were used to prepare the flame retarded epoxy resins. Recently, in consideration of the numerous toxic substance were generated when the halogen flame retardant were burning, and harmful to natural environment and human health [2, 3], the advanced flame retarded epoxy resins are developing toward atendency of halogen-free. As known to all, the mechanical properties of epoxy resin will significantly decrease when using additive flame retardant, while the reactive flame retardant will overcome these defects [4]. Comparing with the preparation of intrinsic flame retarded epoxy resin, the chemical method for synthesizing special hardners containing flame retarded reactive group has many advantages such as simple, easy controllable, it becomes a development tendency to prepare flame retarded epoxy resins with excellent properties. The research on the reactive curing agents containing phosphorus has been reported more and more in recent years. Many amines curing agents containing phosphorus were synthesized by Liu and Döring et al. [5, 6], and have been successfully used in the flame retarded epoxy resin, the level of flame resistance reached UL 94 V-1 and V-0 rating, and the limit oxygen index reached 30-48 when the content of phosphorus was between 2% and

4%. Comparing with the amine curing agents, acid anhydride curing agents has many advantages such as lower volatility, low toxicity, longer usage period, and the cured resins have an excellent electrical property and smaller volumetric shrinkage. Recently, a new environmental friendly flame retardant of cyclic phosphorous compound 9,10-dihydro-oxa-10-phosphaphenanthrene-10-oxide (DOPO) and its derivatives have been reported by many researchers [7-12], and those DOPO-containing epoxy resins exhibit better thermal stability and excellent flame resistance even in a relatively low phosphorus content. Acid anhydride curing agents were the second largest usage amount hardener for epoxy resin, however, the studies on the acid anhydride curing agents containing phosphorus were rarely reported [13-15].

In this chapter, a novel curing agent containing phosphorus of DOPO-based aryl phosphinate dianhydride (BPAODOPE) was synthesized, and flame retarded epoxy resins were prepared by filling BPAODOPE with different phosphorous contents, the flame resistance, thermal properties and mechanical properties of the flame retarded epoxy resins were investigated in detail.

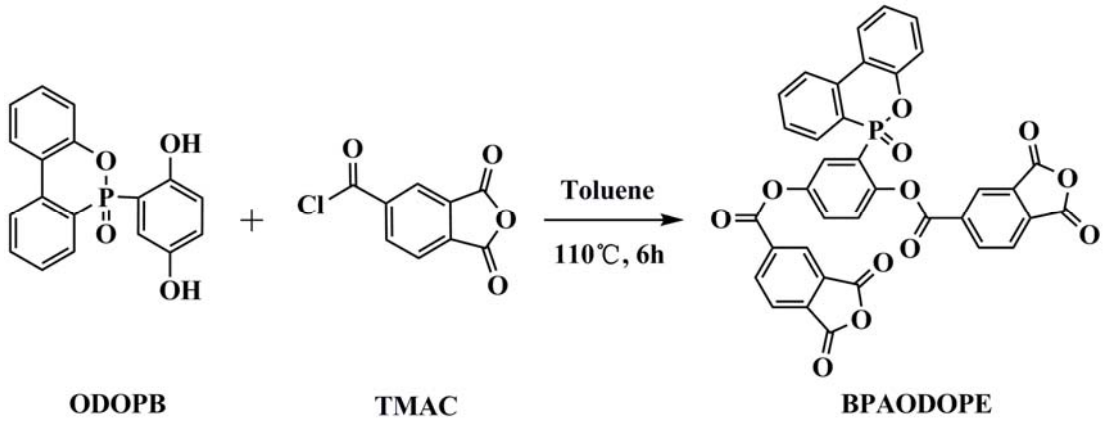
3.2 Experiment

3.2.1 Materials

2-(6-oxid-6H-dibenz<c,e><1,2>oxaphosphorin-6-yl)-1,4-benzenediol(ODOPB), its trade name was DOPO-BQ, obtained from Shandong Mingshan Chemical Industry Company; Trimellitic anhydride acid chloride (TMAC) was reagent grade and used without further purification, supplied by Jiangxi Sanjiang Fine Chemicals Company; Toluene and pyridine were purchased from Sinopharm Chemical Reagent Co., Ltd., toluene was dried with sodium and distilled prior to use, and pyridine used as received.

DGEBA (trade name was E-51) was a kind of epoxy resins and epoxy equivalent was 180-196 g/eq, supplied by Wuxi Resin Factory; Methylhexahydrophthalic anhydride (MeHHPA, hardener) was purchased from Puyang Huicheng Chemicals Co., Ltd.; N-Benzyldimethylamine (BDMA) was used as an accelerator and purchased from Sinopharm Chemical Reagent Co., Ltd.; The other reagents were used as received from commercial sources or purified by standard methods.

3.2.2 Synthesis of BPAODOPE



Scheme 3.1 Synthesis route of BPAODOPE

A 250 mL four-necked round bottom flask was equipped with a thermometer, mechanical stirrer, nitrogen-inlet and reflux condenser with the exhaust pipe. The flask was charged with ODOPB (3.309 g, 0.01 mol), TMAC (6.381 g, 0.03 mol), pyridine (1 ml) and dried toluene (120 ml). The reaction mixture was stirred at room temperature for 1 h, then heated to 110℃, and refluxed for about 6 h in nitrogen atmosphere, the chemical reaction process was shown in Scheme 3.1. After the product was cooled to room temperature of 25℃, the precipitant was filtered and washed with chloroform and ethyl acetate. The crude product was recrystallized from acetic anhydride and dried in a vacuum oven at 100℃ for 6 h, white powders of BPAODOPE were obtained with

93.1% yield, m.p.: 298.8-300.8℃.

3.2.3 Preparation of test samples

Besides synthesized novel hardener Aryl phosphinate dianhydride (BPAODOPE), methyl hexahydrophthalic anhydride (MeHHPA) was also used as a co-hardener, and the mole ratio of anhydride and epoxy groups was 1: 1. In order to compare the results, the curing process of epoxy resin kept in the same conditions in all cases. As shown in Table 3.1, put the hardeners of BPAODOPE and MeHHPA into the epoxy resin (DGEBA) with different mass ratios and mixed uniformly at the temperature of 60℃ for 5 min, and then 0.1 phr BDMA accelerator was added. The mixture was continuously stirred for 5 min and put it into an oven at the temperature of 80℃ for 20 min, then poured the mixtures into some telflon molds at 80℃. The samples were cured at 120℃ for 4 h, and followed by post-curing at 150℃ for 6 h.

Table 3.1 DGEBA samples recipes with different ratio of BPAODOPE/MeHHPA

Samples	P%[a]	DGEBA(g)	BPAODOPE(g)	MeHHPA(g)
EP-1	0	100	0	84
EP -2	1.00	100	44.9	63.3
EP -3	1.50	100	71.5	48.1
EP -4	1.75	100	86.4	41.7
EP -5	2.00	100	102.3	32.9
EP -6	2.25	100	119.0	24.4

Calculated by formula: P%= (weight of BPAODOPE/total weight of the system)×4.61wt%×100%.

3.3 Instrumental analysis and Measurements

3.3.1 Structure analysis

FTIR spectra wererecorded on a Thermo NEXUS-470 Fourier transform infrared spectrometer using KBr pellet. ^{1}H NMR spectra was measured on a Bruker Advance-600 (600 MHz) spectrometer with DMSO-d_6 as a solvent. Melting point of BPAODOPE was measured on a BUCHI B-540 Melting Point Apparatus.

3.3.2 Thermo analysis

The thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed on a NETZSCH (STA449C/41G) thermal analyzer at a heating rate of 10 K/min under N_2 atmosphere. The weights of the tested samples were about 10 mg.

3.3.3 Flame resistance tests

Vertical burning tests (UL 94) were measured on CZF-3 instrument (Jiangning Analytical Instrument Factory, Nanjing) according to ASTM D3801 testing procedure, with sample dimensions of 130.0×13.0×3.0 mm^3. The limiting oxygen index (LOI) was measuredon a JF-3 limiting oxygen index chamber (the same factory with CZF-3) according to ASTM D 2863, with sample dimensions of 130.0×6.5×3.0 mm^3. The percentage of O_2 in the O_2/N_2 mixture was taken as the LOI which was just sufficient to sustain the flame.

3.3.4 Micro-structure analysis

Scanning electron microscopy (JSM-6360LV, JEOL) was used to investigate the residue's surface of neat EP and flame retarded EP. The residues for SEM were the combustion residues of burning samples in vertical burning tests.

3.3.5 Mechanical property tests

According to ISO 527-2, tensile strength tests of 4.0 mm thick samples were tested with TCS-2000 Electric Tensile Tester (Taiwan, China) with a speed of 5 mm/min at room temperature. Charpy impact tests were performed by GT-7045-MDL Charpy Impact Tester (Taiwan, China) according to ISO 179-1. All the listed results were the mean of five samples.

3.4 Results and discussion

3.4.1 Synthesis and characterization

Aryl phosphinate dianhydride BPAODOPE was synthesized by the reaction of trimellitic anhydride acid chloride and ODOPB (Scheme 3.1) with toluene as solvent and pyridine as acid acceptor. The product was purified by recrystallization from acetic anhydride. The FTIR spectrum of ODOPB and BPAODOPE are shown in Fig.3.1.

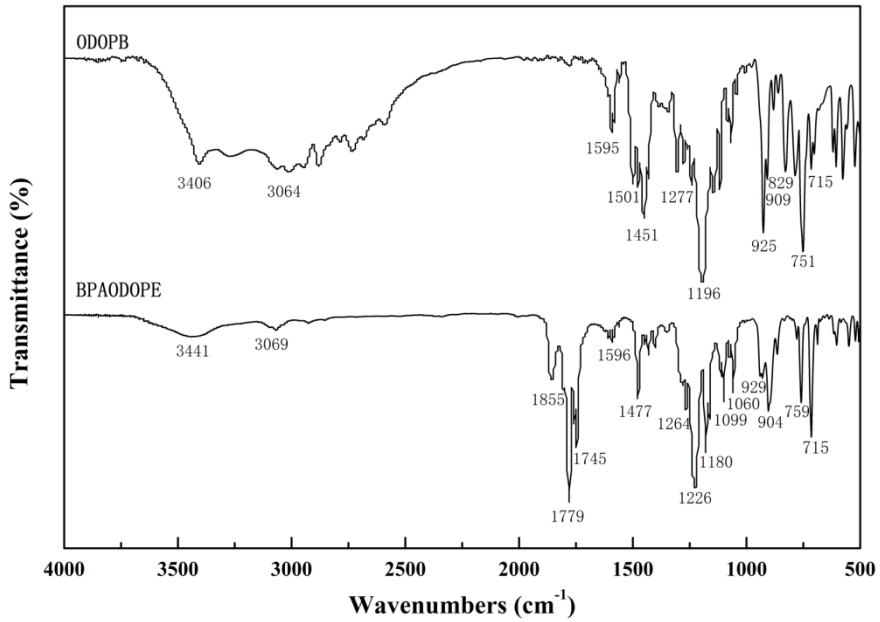


Fig.3.1 FTIR spectrum of ODOPB and BPAODOPE

The characteristic peak at 3000-3500 cm^{-1} (Ar-OH) existed in the crude ODOPB, while it disappeared in BPAODOPE production, and the appearance of characteristic absorption peaks at 1855 and 1779 cm^{-1} were assigned to C=O of anhydride groups, and the peak at 1745 $cm^{-1}$was assigned to the C=O stretching vibration of ester groups. Absorption peaks at 929 and 1180 cm^{-1} were associated with the P-O-Ar groups, and the peak at 1477 cm^{-1} was for the P-Ar groups, the peak at 1264 cm^{-1} was for the P=O groups. Aromatic C-C bond was found at 1596 cm^{-1}, and aromatic C-H absorption was found at 3069 cm^{-1}.

The ^{1}H NMR spectrum of BPAODOPE was shown in Fig.3.2, ^{1}H NMR (DMSO-d_6, ppm): δ= 8.69 (s, 2H); 8.30 (d, J =7.8Hz, 1H); 8.23 (dd, J =14.4Hz, J =2.4Hz, 1H) ; 7.87-7.97 (m, 4H) ; 7.82 (d, J =7.8Hz, 1H) ; 7.65-7.69 (m, 3H) ; 7.56-7.57 (m, 2H) ; 7.36 (t, J =7.2Hz, H) ; 7.22 (d, J =7.8Hz, 1H) ; 7.08(t, J =7.2Hz, 1H). The spectra were in good agreement with the proposed molecular structure. The structure of BPAODOPE was confirmed by FTIR and ^{1}H NMR spectroscopy. Those

results confirmed that the target product was synthesized successfully.

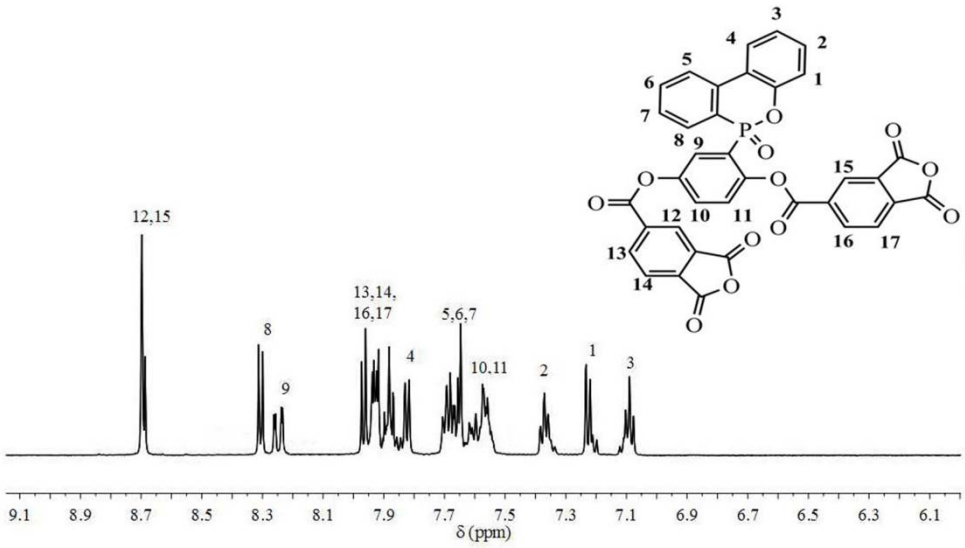


Fig.3.2 ^{1}H-NMR spectrum of BPAODOPE (600MHz, DMSO-d6)

3.4.2 Thermal properties

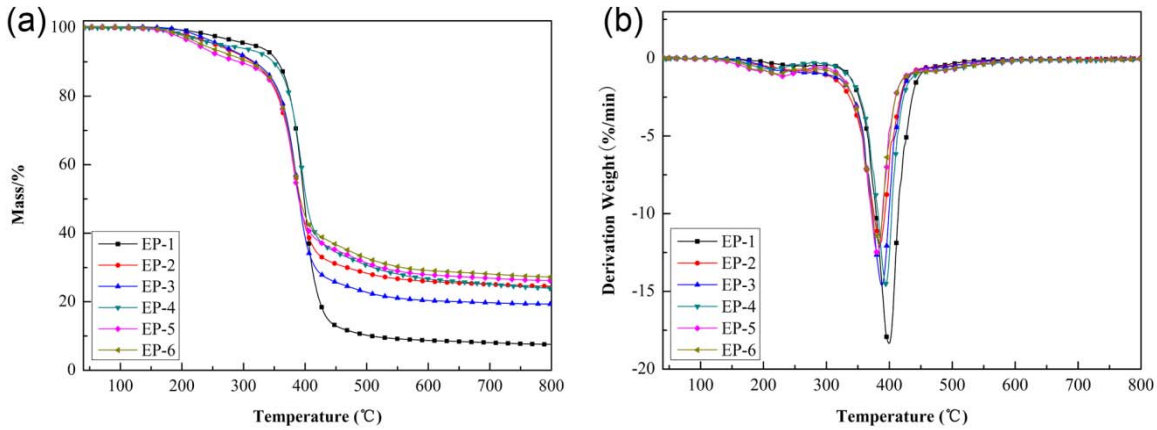


Fig.3.3 TG (a) and DTG (b) curves of the epoxy resin composites with different phosphorus contents

TGA curves and DTG curves of cured epoxy composites under nitrogen are shown in Fig.3.3, and the characteristic values obtained from these curves were listed in

Table 3.2. As shown in Fig.3.3 and Table 3.2, the onset degradation and maximum decomposition temperatures for phosphorus-containing epoxy systems are slightly lower than neat epoxy, the weight loss of the phosphorus-containing epoxy resins were significantly higher than the neat epoxy at 200-300℃, which shows the phosphorus-containing epoxy resin composites has a lower decomposition temperature, the major reason was the phosphorus group degrading at a relatively low temperature(200-280℃), the network's backbone of cured epoxy containing the phosphorus-containing functional groups caused the poorer thermal stability for the weak P-O-C bond decomposition at low temperature [5], this phenomenon was also observed for other phosphorus-containingepoxy resins [16-18].

Table 3.2 Thermogravimetric properties of cured epoxy resins with different phosphorus contents

Samples	P%	Tg (℃)	Temperature of weight loss (℃)			Residue at 800℃
			5%	10%	T_{max}	
EP-1	0	148.7	313.0	355.6	399.5	7.53%
EP-2	1.00	144.9	255.5	313.8	386.8	24.50%
EP-3	1.50	141.2	262.0	317.1	388.2	19.31%
EP-4	1.75	134.0	263.0	348.2	394.6	23.91%
EP-5	2.00	128.6	225.3	293.0	381.4	26.16%
EP-6	2.25	125.4	233.7	308.6	383.3	27.20%

From the Table 3.2, the amount of residual char increased remarkably with an increase of the phosphorus content. The residues of neat epoxy resin was 7.53% at 800℃, while the residues of flame retarded epoxy resin with phosphorous content of

2.25% was 27.20% in the same conditions. The increase of residual char restricts the production of combustible gases, decreases the heat release of the pyrolysis reaction, and reduces the thermal conductivity of the burning materials, consequently, restricts the materials burning further. The thermal stability of epoxy resins was especially affected by the structure of epoxy resin, the type of curing agent, and the curing schedule [19]. The higher char residues of the phosphorus-containing epoxy resin were just caused by phosphorus groups transforming into phosphoric anhydrides and related acid which act as dehydrating agents, and thus promoted char formation [13, 20]. The results indicated that BPAODOPE played an important role in improving the amount of residual char of flame retarded epoxy resins. DSC was used to measure the glass transition temperature (Tg) of cured epoxy resins, the glass transition corresponds to the major value of Tg of the cured epoxy resin, above which temperature significant chain motion takes place. The Tg values of cured samples were listed in Table 3.2, the value of Tg of the neat epoxy was 148.7℃, and those of cured systems with different BPAODOPE contents ranged from 144.9 to 125.4℃. Compared with the neat epoxy resins, the Tg values of epoxy resins containing BPAODOPE decreased significantly, and the more BPAODOPE introduced, the more decrease Tg obtained. This decrease probably came from the remarkable fall of crosslink density, which was in a great part resulting from the opening oxirane reaction that offset the benefit on Tg from the rigid BPAODOPE structure.

3.4.3 Flame resistance

The limiting oxygen index (LOI) can be used as anindicator to evaluate the flame resistance of composite, the LOI values denote the minimum oxygen

concentration required to support downward flame combustion. The LOI values of all samples were listed in Table 3.3.

Table 3.3 Mechanical and flame resistance of the epoxy resins filling with various phosphorus contents

Samples	P%	Tensile strength (MPa)	Impact strength (kJ/m^2)	UL 94	LOI
EP-1	0	37.90	5.19	Failed	19.8
EP-2	1.00	34.89	4.03	Failed	25.4
EP-3	1.50	32.44	3.76	V-1	27.6
EP-4	1.75	30.78	3.53	V-0	29.3
EP-5	2.00	28.90	3.25	V-0	29.9
EP-6	2.25	27.86	2.85	V-0	30.6

It can be seen that the LOI values significantly increase from 19.8 to 30.6 with the phosphorus content increasing from 0 to 2.25 wt%, which indicates that the phosphorus-containing BPAODOPE is very effective inimproving the flame retardation of epoxy resins. The vertical burning test (UL 94) determines the upward burning characteristics of the polymer. It is clear that the flame retardation of cured epoxy resins increases with an increase of phosphorus content, and UL 94 V-0 rating can be obtained by phosphorus content of 1.75 wt%. The results showed that the flame retarded epoxy resin can be prepared by incorporating BPAODOPE with minimum phosphorus content of 1.75%.

3.4.4 Morphology of residual char

The morphologies of four char residues have been observed by SEM, as shown

in Fig.3.4.

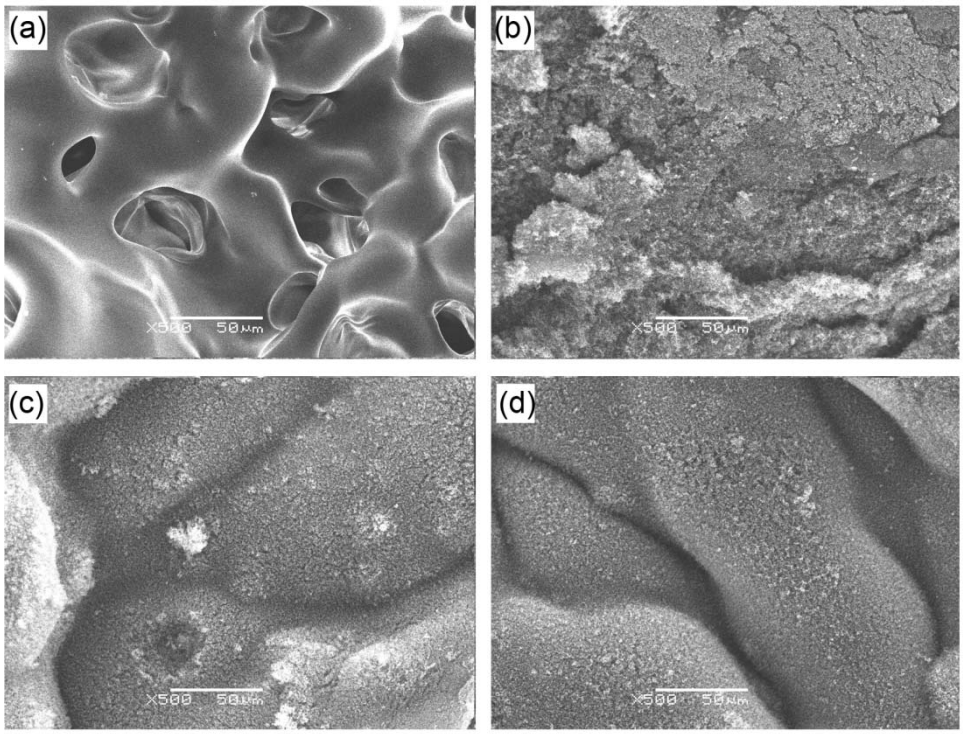


Fig.3.4 SEM morphology of the residues of samples, (a) EP-1, (b) EP-2, (c) EP-4, (d) EP-6

After the neat epoxy (named EP-1) burned, as shown in Fig.3.4 a, there are numerous pores, and the pores acted as the channels through which oxygen and the fuel flowing and interacting, thus contributing to combustion, and there are no flame retardation char layers existing in the surface of residue. However, the compact char layers can be observed on the residues surface of the flame retarded epoxy resins, which was shown in Fig.3.4 b-d, the char layers effectively protect the internal structures of samples, inhibit the heat transmissionand reduce the fuel gases in the combustion process. Incompact char layers were observed in the residue surface with phosphorus content of 1.00% in Fig.3.4 b; when the phosphorus content increased to 1.75% and 2.25%, as shown in Fig.3.4 c and d, the compact intact char layers formed

on the residue surface, which prevented the combustion of epoxy resins effectively. Therefore, flame retarded epoxy systems containing BPAODOPE showed a good flame resistance. Those results were in accordance with the results of TGA, LOI and UL 94 testing. The formation of char layer demonstrated that phosphorus of BPAODOPE played an important role. During combustion, phosphorus in polymers converted to phosphoric acid, and further thermal decomposition leaded to the formation of polyphosphoric acid. The polyphosphoric acid esterified and dehydrated the pyrolyzing polymers, and formed phosphorus-rich char layers simultaneously, which inhibited the pyrolysis reactions further. The protective layers restricted the heat transmission and provided a good flame shield for the underlying material during combustion [21].

3.4.5 Mechanical properties

The mechanical properties of the cured epoxy resins were characterized by vertical drawing test and charpy impact test. The results were shown in Table 3.3. Flame retarded epoxy resins exhibited lower tensile and impact strengths than neat epoxy resin. Compared with neat epoxy resin, mechanical properties of flame retarded samples gradually decreased with an increase of BPAODOPE. Tensile strength and impact strength of neat epoxy resin were 37.90 MPa and 5.19 kJ/m^2, however, the corresponding strength values of flame retarded sample dropped to 27.86 MPa and 2.85 kJ/m^2 when filling BPAODOPE with phosphorous content of 2.25%, the tensile strength dropped 26.5%, and impact strength dropped 45.1% than the neat epoxy resin respectively. The mainly reason for the mechanical strength decreasing was just for the excessive filling of BPAODOPE, meanwhile, the BPAODOPE has a lower phosphorous

content and a rigid molecular structure, the steric hindrance effect caused by the rigid structure will decrease cross-linking density of epoxy resins, which deteriorates the mechanical properties of flame retarded epoxy resins. The conclusion can be drawn that the reactive flame retardant BPAODOPE improved the flame resistance of epoxy resin obviously, while the mechanical properties had a certain decline. Considering the combination properties of flame retarded epoxy resin, the sample of EP-4 with phosphorous content of 1.75% has the best performance, tensile strength and impact strength were 30.78 MPa and 3.53 kJ/m^2, LOI value was 29.3, and the vertical burning test reached UL 94 V-0 rating.

3.5 Conclusions

In this chapter, a novel aryl phosphinate dianhydride BPAODOPE was synthesized successfully, and used as hardener and flame retardant for preparing halogen-free flame retarded epoxy resins when coupled with another curing agent. The epoxy resin composites filling with BPAODOPE had excellent flame resistance and higher char yield, and the flame resistance and char yields of the flame retarded epoxy resins increased with an increase of phosphorus content. And the epoxy resins with the phosphorus contents of 1.75% showed excellent combination properties. The results also show that BPAODOPE has some shortcomings, it has a lower phosphorous content, when the phosphorous content is 2.25%, the mechanical properties of epoxy resin will decrease obviously, tensile strength and impact strength of the sample were 73.5% and 54.95% for their values of neat epoxy resin respectively. So the further study will focus on the synthesis of some novel reactive flame retardants, which should have a higher phosphorous content of unit mass, and improve the combination properties of flame retarded epoxy resins.

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Chapter 4

Synthesis of novel flame retardant PES and its application in epoxy resin

4.1 Introduction

The epoxy resin has been widely used for its excellent mechanical, electrical performance and chemical resistance, however, the combustion of pure epoxy resin limits its application, especially in some electrical materials, therefore, it has been become the research topic of how to improving the flame resistance of epoxy resin and preparing halogen free flame retardants for epoxy resin for the environmental pollution of halogen flame retardants [1-3]. As for the much more advantages of phosphorous containning flame retardant and curing agent, compared with additive traditional flame retardants, it can effectively avoid the great loss of mechanical performance, so the phosphorous containning flame retardant and curing agents have been focused in recent years. In this field, Isara Jirasutsaku [2] et al. synthesized two kinds of aromatic diamine epoxy resin flame retardant and curing agent, PPEDD and PPPDD. When the epoxy resin filled the curing agent with the phosphorous content of 2-3%, the LOI values of the composites by PPEDD and PPDD enhanced from 20 (cured by ethylene diamine) or 21 (cured by p-phenylenediamine) to 27 and 31 respectively. In order to develop novel flame retardants of epoxy resin with halogen free, high efficiency, and less loss in mechanical performance, the author attempts to synthesize PES with high phosphorous content by using pentaerythritol, $POCl_3$ and ethylene diamine, the synthesized PES can react with epoxy resin to prepare flame retarded epoxy resin with high mechanical performance. The LOI, vertical buring test (UL 94), thermogravimetric analysis (TG)

and scaning electron microscopy (SEM) were used to characterize the corresponding flame retardance and thermal resistance of flame retarded epoxy resin composite, and the flame retardance mechanism was also discussed in detail.

4.2 Experiment

4.2.1 Materials

All of the starting materials and solvents were commercially available and were used without further purification. Pentaerythritol (PER), ethylene diamine, acetonitrile, chlorobenzene, 4,4-diamino diphenyl sulfone (DDS), triethylamine and dichloromethane (CH_2Cl_2; analytical reagent) were purchased from Sinopharm Chemical Reagent (Liaoning, China). Phosphorus oxychloride ($POCl_3$, AR), and 4-pryidinemethaneamine (chemically pure) were purchased from Chengdu Geleixiya Chemical Co. Ltd (China). Allyl glaycidyl ether (AGE, industrial grade) was obtained from Gao chemical (Shanghai) Internation Trade Co. Ltd.. The EP resin (bisphenol A diglycidyl ether, trade name E-51, EP equivalent = 180-196 g/eq) was purchased from the Wuxi Resin Factory (Jiangsu, China). Nitrogen gas was industrial grade, the content was higher than 98.5%.

4.2.2 Synthesis of SPDPC

First, 54.46 g of PER (0.4 mol), 96.9 ml of $POCl_3$ (1.04 mol), 250 ml of chlorobenzene, and 0.2 g of DMAP (catalyst) were mixed in a 500 ml glassflask equipped with a condenser, a N_2 inlet, a thermometer, a magnetic stirring bar, and a gas absorber. The mixture was stirred at 60°C for 2 h; then, the reaction temperature was elevated to 100°C, and the reaction was protected with N_2 gas and kept for 8 h. After the

reaction, the N_2 must be continued until the room temperature was reached. The product was filtered and purified with distilled water and CH_2Cl_2 sequentially and then dried to aconstant weight at 80°C under vacuum. A white solidpowder was obtained (yield: 90%) **[**4-7**]**. The relative chemical reaction process is shown in Fig.4.1.

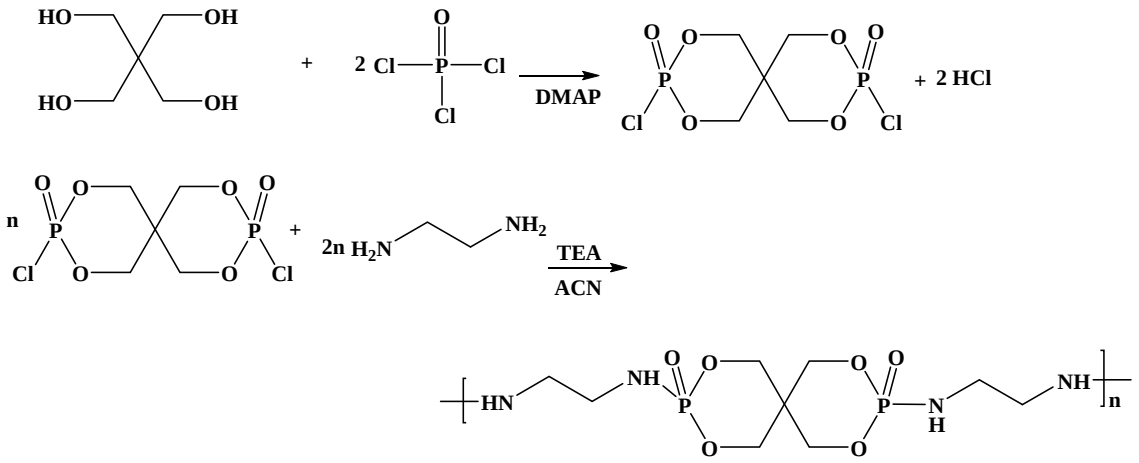

Fig.4.1 The synthetic route of PES

4.2.3 Synthesis of PES

Spirocyclic pentaerythritol bisphosphorate disphosphorylchloride (SPDPC; 44.54 g, 0.15 mol) and 41.8 ml of triethylamine were dispersedin 300 ml of acetonitrile and transferred to a glass flask. Ethylene diamine (20.1 ml, 0.3 mol) and acetonitrile (20 ml) were dropped by using a pressure-equalizing dropping funnel, the whole dripping process was kept for 2 h, and enhanced the reaction temperature to 60℃ and reacted for 6 h. The product was filtered and purified by ethanol and then dried to a constant weight at 80℃ under vacuum. White solid PES powder was finally obtained (yield: 95%) [8,9].

4.2.4 Preparation of flame-retarded EP composites

A certain amount of pure epoxy resin was weighed and put into 100 ml beaker,

and added into few AGE, and heated to 90℃, the mixture liquid was stirred and filled with PES flame retardant, when the mixture was dispersed uniformly, the curing agent DDS was added, the mixture was placed into an oven at 120℃ and stirred continuously for 20 min, then degased for 40 min at 80℃. The mixture was poured into a Telflon model at 120℃ and pre-cured for 2 h, then post-cured for 6 h at 150℃, the yellow flame retarded epoxy resin composite samples were obtained successfully. The specific contents of different components were listed in Table 4.1.

Table 4.1 Different phosphorus content of epoxy resin composite materials

Samples	P%	DGEBA(g)	PES(g)	DDS(g)	AGE(g)
EP-0	0	100	0	40	10
EP-1	2.90	100	25	20	10
EP-2	3.48	100	30	15	10
EP-3	4.06	100	35	10	10

P%= $(m_{(PES)}/m_{total})\times 18wt\%\times 100\%$, (18% was the phosphorous content in PES)

4.3 Instrumental analysis and measurements

4.3.1 Structure analysis

FTIR spectra were recorded on a Thermo NEXUS-470 Fourier transform infrared spectrometer using KBr pellet. The ^{1}H NMR spectra was measured on a Bruker Advance-600 (600MHz) spectrometer with DMSO-d_6 as a solvent.

4.3.2 Heat resistance

The thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed on a NETZSCH (STA449C/41G) thermal analyzer at a heating rate of 10 K/min under N_2 atmosphere. The weights of the tested samples were about 10

mg.

4.3.3 Flame resistance tests

Vertical burning tests (UL 94) were measured on CZF-3 instrument (Jiangning Analytical Instrument Factory, Nanjing) according to ASTM D3801 testing procedure, with sample dimensions of 130.0×13.0×3.0 mm^3. The limiting oxygen index (LOI) was measuredon a JF-3 limiting oxygen index chamber (the same factory with CZF-3) according to ASTM D 2863, with sample dimensions of 130.0×6.5×3.0 mm^3. The percentage of O_2 in the O_2/N_2 mixture was taken as the LOI which was just sufficient to sustain the flame.

4.3.4 Micro-structure analysis

Scanning electron microscopy (JSM-6360LV, JEOL) was used to investigate the residue's surface of neat EP and flame retarded EP. The residues for SEM were the combustion residues of burning samples in vertical burning tests.

4.3.5 Mechanical property tests

According to ISO 527-2, tensile strength tests of 4.0 mm thick samples were tested with TCS-2000 Electric Tensile Tester (Taiwan, China) with a speed of 5 mm/min at room temperature. Charpy impact tests were performed by GT-7045-MDL Charpy Impact Tester (Taiwan, China) according to ISO 179-1. All the listed results were the mean of five samples.

4.3.6 ESI-MS

The LCQ Deca XP typed Liquid Chromatography-Mass spectrum (US, thermo) was used for the characterization of sample.

4.4 Results and discussion

4.4.1 FTIR characterization of PES

The FTIR spectrum of PES is shown in Fig.4.2. In the spectrum of SPDPC, the characteristic peak at 2988 cm^{-1} and 1308 cm^{-1} are corresponding to the stretching vibration of C-H and the feature adsorption peak of P=O respectively. The peak at 1027 cm^{-1} corresponds to the feature adsorption peak of P-O-P, the peak at 854 cm^{-1} is the adsorption peak of P-O, the peak at 549 cm^{-1} is the adsorption peak of P-Cl. While in the spectrum of PESPB, the peaks of 3405, 3199, 1609 cm^{-1} are assigned to the feature adsorption peaks of $-NH_2$, the peak at 1236 cm^{-1} is the adsorption peak of P=O, the feature adsorption peaks of P-O-P ad P-N appear at 1018 cm^{-1} and 1075 cm^{-1}, and the featured peak at 549 cm^{-1} of the P-Cl bond in SPDPC disappear in the spectrum of PESPB, the new featured peak of P-N appears at 1075 cm^{-1}, considering the change, the reaction was considered taking place between SPDPC and EDA, and the PESPB is produced finally.

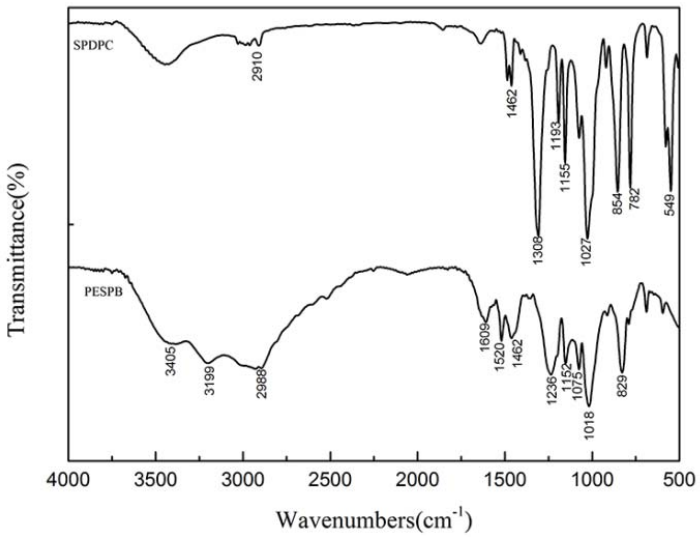

Fig.4.2 FTIR spectra of SPDPC and PESPB

4.4.2 The ^{1}HNMR characterization of PES

The PES structure was characterized by ^{1}H NMR spectrum, shown in Fig.4.2, the chemical shift δ of hydrogen atom of PES was given, δ= 2.07 ppm (-NH_2), 2.50 ppm (the H in solvent DMSO-d^6), 2.80-3.10 ppm (-CH_2-) ,4.20-4.40 ppm (-CH_2- in spiral structure), as for the reactive hydrogen in its structure, there will be some errors in the specific chemical shifts, and the solvents also induce the change of peak position, however, the spectrum is corresponding with the construction of PES compound.

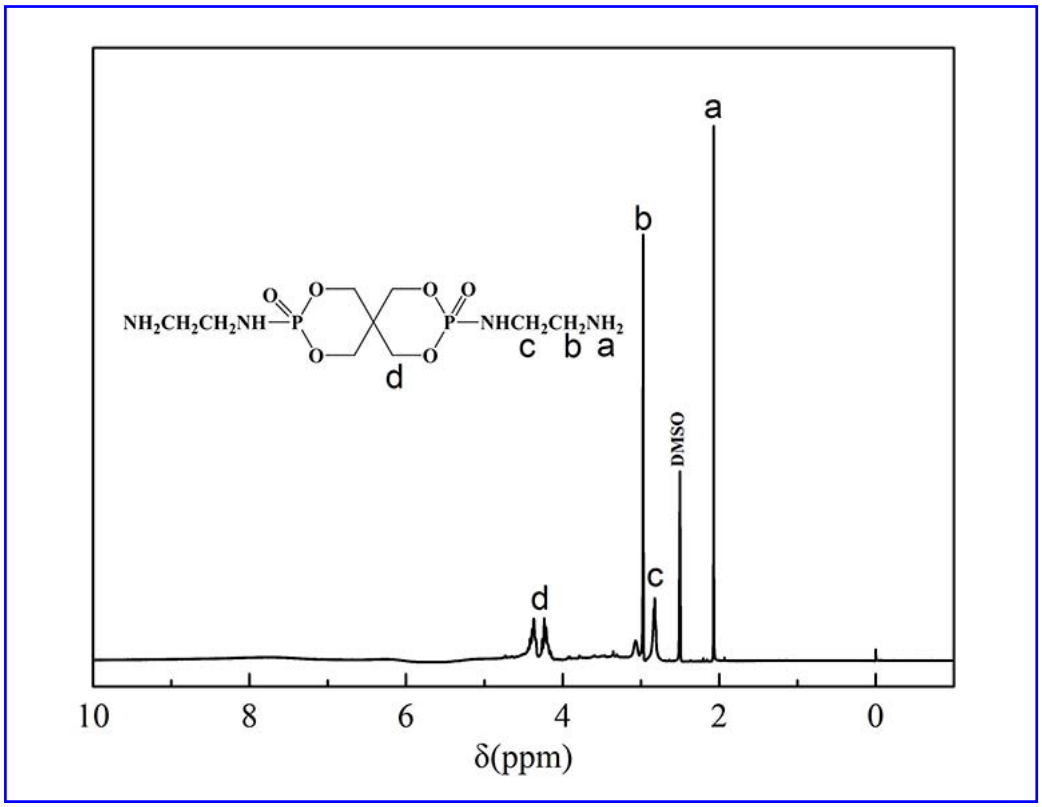

Fig.4.3 [1]HNMR spectrum of PES

4.4.3 The ESI-MS characterization of PES

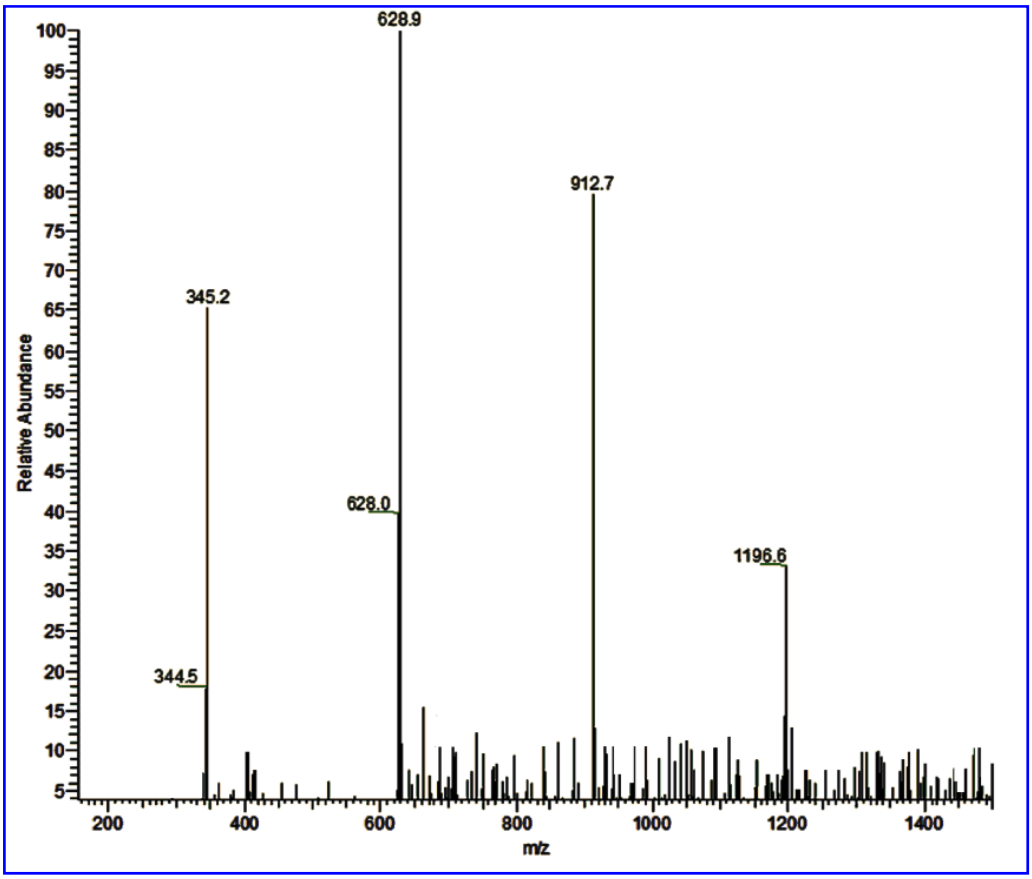

Fig.4.4 Mass spectrum of PES

The theory of mass spetrum analysis is based on the mass measurement of molecules, ions and fragment ions of samples under high vacuum system, and confirmed the molecules weight and their molecular structures of samples. When the compound molecules are impacted by the electron beams, the positive molecules, ions and fragment ions can be formed, the spectrum is recorded by the value of m/z (m denotes the mass of sample, z denotes the charge) according to the value order. The mass spectrum of PES is shown in Fig.4.4, the values of m/z 345.2, 628.9, 912.7 and 1196.6 are corresponding to the structures of MH^+, M_2H^+, M_3H^+, M_4H^+, and the repeated unit structure of PES is given in Fig.4.1. The results of Mass spectrum are well

agreement with the theoretical structure of PES, and combined the results of FTIR and ^{1}HNMR, the predicted PES has been confirmed to be synthesized successfully.

4.4.4 The characterization of thermal property

TGA curves and DTG curves of PES under air are shown in Fig.4.5, the onset degradation temperature of PES is 288.6℃. Two decompositon phases can be divided from the weight loss curve, the first phase is located in 296.1℃~573.9℃, and the maxmum weigh loss temperature is about 310℃, and the weight loss is 63.01%. The second phase is beginning from 573.9℃, and the largest weight loss temperature is about 620℃, the residual char is 8.32% at 800℃. The aboved results show that the initial decomposition temperature of PES is fit for the preparation of flame retarded epoxy resins.

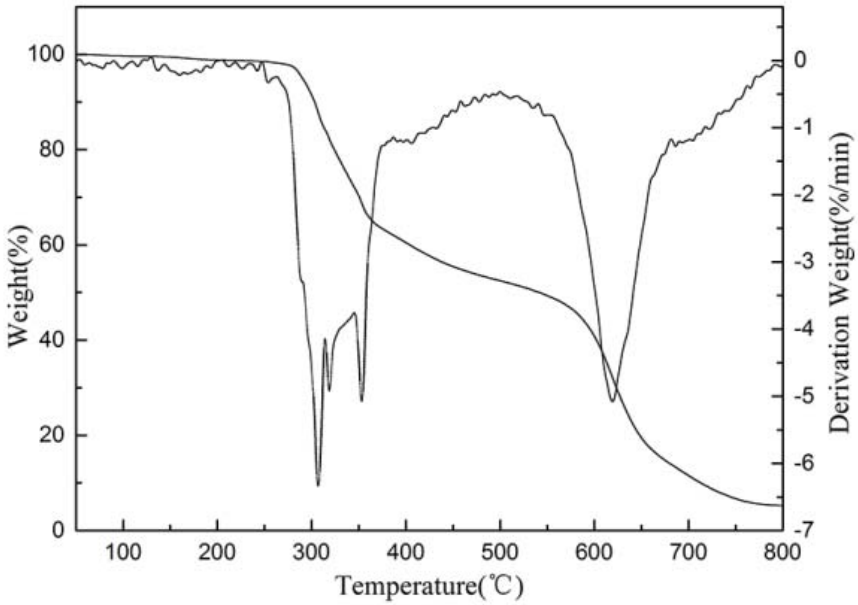

Fig.4.5 TG-DTG curve of PES at air atmosphere

4.4.5 The heat resistance and flame resistance of EP/PES/DDS

TGA curves and DTG curves of cured EP/PES/DDS composite under nitrogen are shown in Fig.4.6 and Table 4.2, the onset degradation temperature of EP/PES/DDS systems is slightly lower than pure epoxy (EP), the weight loss at 280℃~400℃ of EP/PES/DDS is higher thanpure epoxy, which shows the phosphorus-containing epoxy resin composites has a lower decomposition temperature. The major reason is the phosphorus group decomposing at a relatively low temperature (200-280℃), the network's backbone of cured epoxy containing the phosphorus-containing functional groups caused the poorer thermal stability for the weak P-O-C bond decomposition at low temperature, this phenomenon is also observed for other phosphorus-containing epoxy resins [10,11].

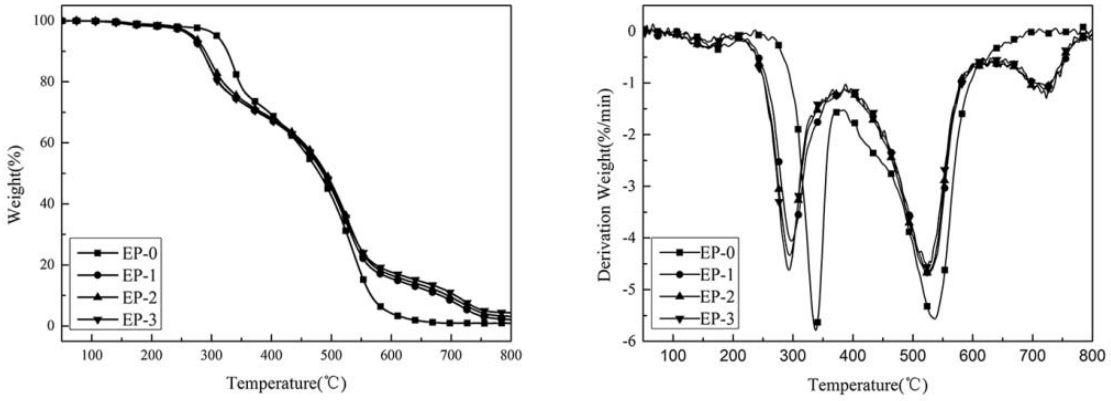

Fig.4.6 TG-DTG curves of flame retarded epoxy resin composite in the air

Table 4.2 Thermal analysis data of EP/PES/DDS curing system

Samples	P%	Temperature of weight loss (℃)				Residue	
		T_{onset}	$T_{10\%}$	T_{max1}	T_{max2}	600℃	800℃
EP-0	0	309.12	326.29	338.01	533.31	4.18%	0.68%
EP-1	2.90	269.97	289.42	296.02	530.40	15.27%	2.12%
EP-2	3.48	264.94	284.35	294.56	524.59	16.92%	3.27%
EP-3	4.06	262.40	282.62	293.11	524.31	17.67%	4.42%

From the Table 4.2, the amount of residual char increased remarkably with an increase of the phosphorus content. The char residues of pure epoxy resin was 4.18% and 0.68% at 600℃ and 800℃, while the char residues of flame retarded epoxy resin composite with phosphorous content of 4.06% was 17.67% and 4.42% at the same temperature. The possible reason is that the addition of PES into EP, when the composite is decomposed at higher temperature, the phosphorus containning acid can be produced, which plays a positive role in dehydration and pyrolyzing char, meanwhile, the nitrogen elements change into nitrogen containning inert gas, which dilutes the concentration of oxygen gas in air and reduces the heat release from pyrolytic reaction, finally forms compact char layer to decrease the thermal conductivity of buring materials, and the flame retardance can be achieved successfully.

Table 4.3 The mechanical properties and flame retardant performanceof flame retardant epoxy resin composite materials

Samples	P%	Tensile strength (MPa)	Impact strength (kJ/m^{-2})	LOI	UL 94
EP-0	0	79.41	8.44	20.3	Failed
EP-1	2.90	68.64	6.37	26.6	V-1
EP-2	3.48	62.76	6.81	28.9	V-0
EP-3	4.06	59.48	5.63	30.5	V-0

The mechanical properties and flame retardance of different samples were characterized by vertical drawing test, charpy impact test, vertical buring and limited oxygen index testing. The results were shown in Table 4.3. Flame retarded epoxy resins exhibited lower tensile and impact strengths than pure epoxy resin sample. Compared with neat epoxy resin, mechanical properties of flame retarded samples gradually decreased with an increase of PES. Tensile strength and impact strength of flame retarded compositeare 62.76 MPa and 6.81 kJ/m^2 with the phosphorous content of 3.48%. The mainly reason for the mechanical strength decreasing was just for the poor dispersion of PES particles in epoxy resin, meanwhile, the PES acts as fillers when the resin cured, the AGE reactive diluent was added for the higher viscosity caused by PES particles, so the addition of diluent aslo decreased the mechanical performance of flame retarded composite. The less addition of DDS can reduce the crosslinking density of epoxy resin, which drops the mechanical performance of flame retarded composite. Meanwhile, the PES has ahigher phosphorous and nitrogen content and a rigid molecular structure, the steric hindrance effect caused by the rigid structure will decrease cross-linking density of epoxy resins, which deteriorates the mechanical properties of flame retarded epoxy resins [12].

The limiting oxygen index (LOI) is an indicator to evaluate the flame resistance of polymer, the LOI values denote the minimum oxygen concentration required to support downward flame combustion. The LOI values of all samples were listed in Table 4.3. It can be seen that the LOI values significantly increase from 20.3 to 30.5 with the phosphorus content increasing from 0 to 4.06 wt%. The vertical burning test (UL 94) determines the upward burning characteristics of the polymer. It is clear that the flame retardance of cured epoxy resin composites increases with an increase of

phosphorus content, and UL 94 V-0 rating can be obtained by phosphorus content of 3.48 wt%. The aboved results indicate that the synthesized PES can improve the flame retardance of epoxy resins and has a higer flame retardant efficiency.

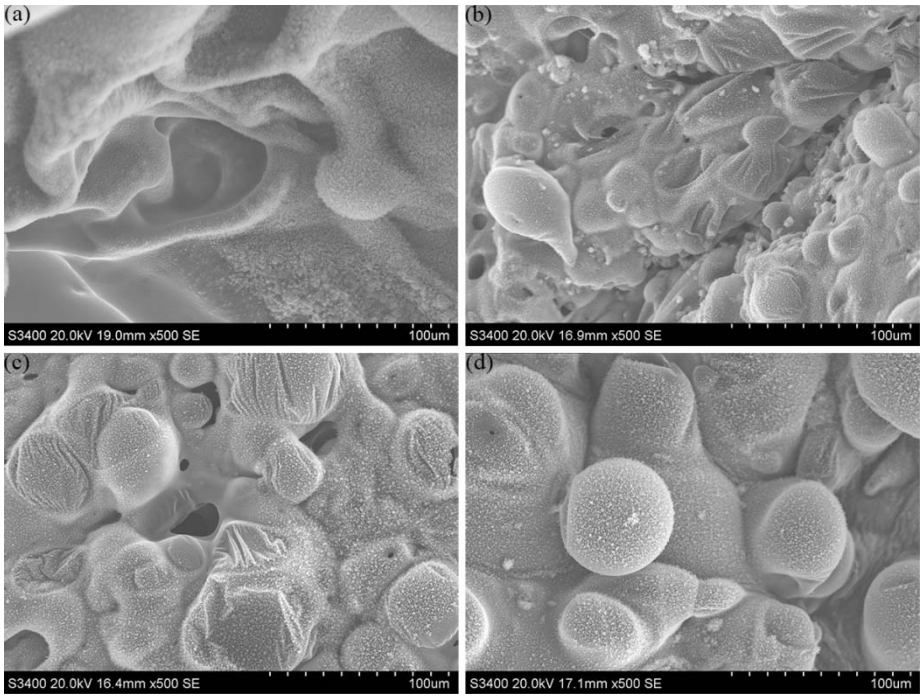

Fig.4.7 Different samples of residual carbon layer scanning electron microscopy: (a) EP-0; (b) EP-1; (c) EP-2; (d) EP-3

In order to research the flame retardance mechanism, the residual char surfaces of pure epoxy resin and flame retarded composites were characterized by SEM, and the pictures were given in Fig. 4.7. The residual char of pure epoxy resin is shown in Fig.4.7a, there are numerous loosened pores in rough surface. The residual char surface of flame retarded composites with different contents of PES is shown in Fig.4.7 (b-d), when epoxy resin was filled with different fraction of flame retardant, there are lots of swelling pores, and compact char layer formed on the surface of pores, with an increase of flame retardant content, the char layer will become more compact, which can be seen from Fig. 4.7d. Much more researches show that the compact char layer can isolate

flame and retard the heat transmission from outside heat source to the internal of polymer matrix, the flame retardant contains nitrogen elements, when heated the decomposition inert gas will insulate oxygen gas and combustible gas, which avoids the contact between gas and polymer matrix, and effectively retard the further burning of polymer. Moreover, PES aslo contains much more phosphorus elements, the polyphosphorus acid or metaphosphorus acid can be produced from the decomposition of flame retardant, and dehydrates the composite and produces high temperature water vapor, which induces the swelling of residual char and prevents the spreading and transfering of flame. The water vapor dilutes the concentration of combustible gases and slows down the buring rate.

Considering the combination properties of flame retarded composite, the sample with phosphorous content of 3.48% had the best performance, tensile strength and impact strength were 62.76 MPa and 6.81 kJ/m^2, LOI value was 28.9, and the vertical burning test reached UL 94 V-0 rating.

4.5 Conclusions

A novel phosphorus containning flame retardant and curing agent PES was synthesized successfully with pentaerythritol, phosphorus oxychloride and ethylene diamine, the structure and performance of production was characterized by using FTIR, ^{1}HNMR, ESI-MS and TG. The synthesized PES and DDS was used as flame retardant and curing agent, and the flame retarded epoxy resin composites were prepared with different phosphorus content. The TG results showed that the addition of PES decreased the initial decomposition temperature of epoxy resin, and the residual char of composites increased with an increase of PES fraction at 800℃. The residual char

suface of flame retarded composite was observed by SEM, and the results show that the swell and compact char lay can be formed after the addition of PES. The flame retarded composite with the phosphorous content of 3.48% shows the best combination performance, the limited oxygen index increases from 20.3 to 28.9, and reaches UL 94 V-0 rating, the tensile strength and impact strength of thissample are 62.76 Mpa and 6.81 kJ/m^2 respectively. Although the addition of PES weaken the mechanical performance of composite, it can greatly improve the flame retardance of epoxy resin, considering the combination performance of flame retarded composite, the synthesized phosphorus containning PES has a promising application prospect.

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Chapter 5

Synthesis of intumescent flame retardant PDEPDMand its application in polyethylene

5.1 Introduction

The polymer materials are extensively applied in industry, agriculture, and daily lifeowing to their good mechanical properties, processing properties and chemical stability [1]. However, their applications are limited in different degree, because most of them are not flame materials. Therefore, the smoking and environmental pollutions of flame retardants in polymer materials have brought attention to the development and applications of new generation chemistry products by both research scientists and industry, and the new high-performance flame retardant with low cost and higher efficiency have been considered to be designed or produced [2].

The phosphorus-based and nitrogen-based flame retardants were widely used in the macromolecule materials, they have both different flame effect, different phosphorus-based flame retardants have been used such as red phosphorus, inorganic phosphates and organic phosphorus-based products. Phosphorus flame retardants are significantly more effective in nitrogen or oxygen-containing polymers, which could be either heterochain polymers or polymers with these elements in pendant groups. Effective phosphorus flame retardants are more specific than halogen-based products to certain polymers. Recently, organic phosphorus compounds have used in the macromolecule materials for many years [3-5], it showed good ability in flame retardant and generated less toxic gas and smoke than other compounds. In recent years,

traditional halogen flame retardants have been challenged as the results of the ecological problems, and halogen-free products are playing more and more important roles. However the nitrogen-based flame retardants applied in macromolecule materials and include inorganic nitrogen and organic nitrogen products, the melamine cyanurate (MCA) of organic nitrogen products shows some remarkable advantages including high nitrogen content, satisfactoryflame retardancy, non-corrosion and innocuity. The applications of MCA in flame retardant macromolecule materials were reported early in 1970. Furthermore, scientists found that a synergistic effect can be considered to improve the flame resistance efficiency. The phosphorus-based and nitrogen-based flame retardants, when used together, exhibit synergistic flame retardation effects.

It is well-known that intumescent flame retardants (IFR) are efficient in some polymers and are widely used as halogen-free additives owing to their advantages of little smoke and low toxicity. So IFRs have attracted much attention to researchers and engineers worldwide. The IFR system usually endures an intense expansion and forms protective charred layers, thus well protecting the underlying material from the action of the heat flux or flame during combustion. An IFR system is made of three components: an acid source, a carbon source, and a blowing source. In this paper, the P-N intumescent flame retardant was prepared and added into the PE to test the flame effect, and the polymer was analyzed by Fourier Transform Infrared Spectrometer (FTIR) and Nuclear Magnetic Resonance (NMR), thermogravimetric analysis (TG), flame retardant properties of PE were investigated by limiting oxygen index (LOI). Through this research, we hope to provide an efficient intumescent flame retardant technique with excellent flame resistance efficiency.

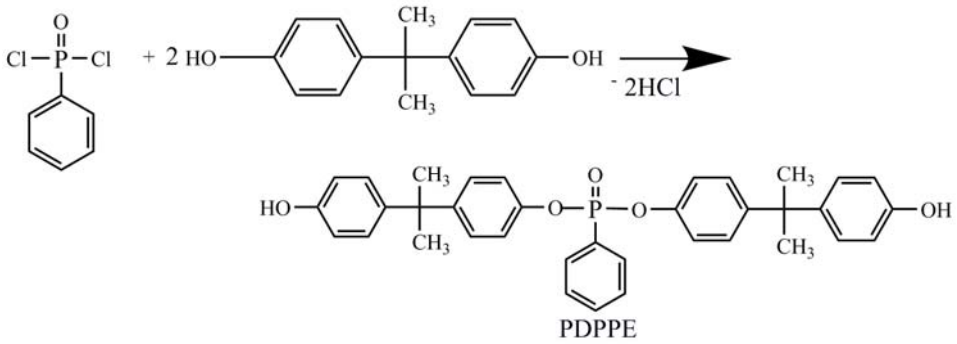
5.2 Experiment

5.2.1 Materials

Bisphenol A (BPA, CP) and phenyl phosphonicdichloride (PPD, CP) werechemically pure and purchased from Sinopharm Chemical Reagent Co., Ltd, Beijing, China; melamine (MA, AR) was analytical reagent and obtained from Damao Chemical Reagent Factory, Tianjin, China; triethylamine (TA, AR), acetonitrile (AI, AR)and dichloromethane (DCM, AR) were analytical reagent and purchased from Tianjin Bodi Chemical Co., Ltd, Tianjin, China.

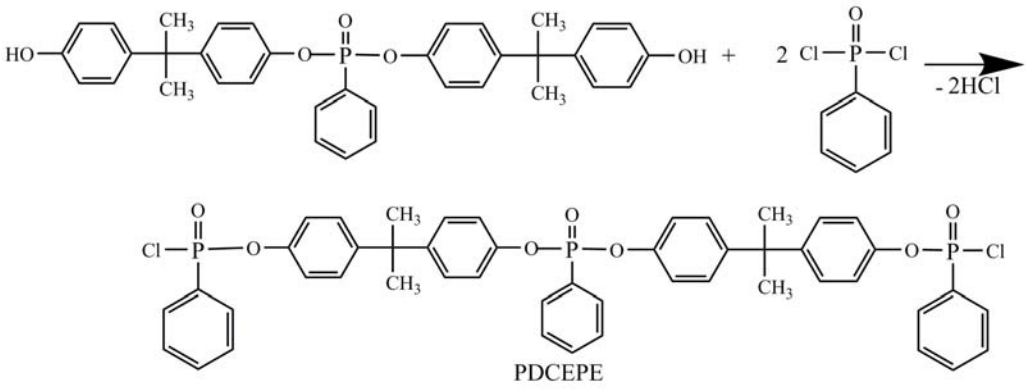
5.2.2 Synthesis of intermediate product PDPPE and PDCEPE

Firstly, 0.022 moL BPA, 0.022 moL TA and 10 mL AI were put into a 100 mL three-necked flask equipped with a magnetic stirrer, condenser pipe, thermometer and constant pressure funnel. The mixtures were stirred for minutes, when the temperature reached 8°C, 1.950 g PPD was added into the three-necked, the reaction was kept at 8^{o}C for 4 h, then the reaction solution was poured into the beaker, The final solution was filtered and dried at 60°C in a vacuum oven, the intermediate product of PDPPE was obtained successfully. The reaction process above was shown in Scheme5.1.



Scheme 5.1 Synthesis route of PDPPE

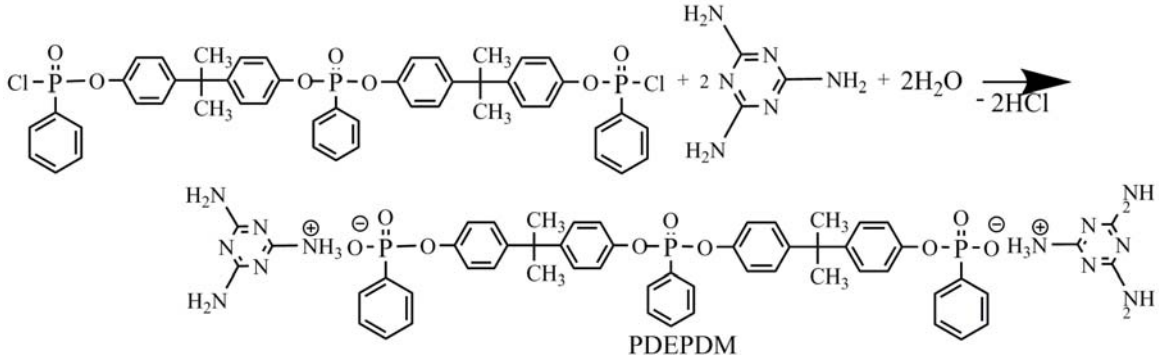
Secondly, the next intermediate product of PDCEPE was synthesized as follows, 0.01 moL PDPPE, 0.022 moL PPD and 20 mL AI were added into a 100 mL three-necked flask equipped with a magnetic stirrer, the mixture were stirred at 80°C for 10 h, then the solution changed into milk white and filtered, and the solid powder was dried at 60°C for 12 h in vacuum. The reaction schematic was shown in Scheme 5.2.



Scheme 5.2 Synthesis route of PDCEPE

5.2.3 Synthesis of PDEPDM

The reaction process was shown in Scheme 5.3 and the detailed information listed as follows: 0.0132 mol MA and 0.006 mol PDCEPE were crushed into powders and put into a 100 mL three-necked flask, the mixture were stirred for 4 h at 90°C. Finally, the final product of PDEPDM were filtered, dried at 90°C for 12 h in vacuum and stored in desiccators to keep dry.



Scheme 5.3 Synthesis route of final product PDEPDM

5.2.4 Characterization

FTIR spectrum of PDPPE, PDCEPE and PDEPDM powders were collected on NEXUS-470 (Thermo Nicolet Corporation, American) by using KBr pellets technique. ^{1}H and ^{31}P-NMR were performed on a Bruker Avance 500 MHz spectrometer by using DMSO as solvent and tetramethylsilane (TMS) as a reference respectively. Thermogravimetric analysis (TG) was collected from 5 mg samples under air atmospheres at a heating rate of 10°C/min by using STA 449C thermogravi-metric analyzer (Beijing Heng Odd Instrument Co., Ltd. China). Limiting Oxygen Index (LOI) value were measured by Fire Testing Technology Instrument (Suzhu Qile Electronic Technology Co., Ltd. China) at a flow rate of 10 L/min with the specimen bars of 120mm×6.5mm×3.2 mm in length, width and thickness respectively. The Burning morphology of the samples was charactered by scanning electron microscope (SEM, S-3400N, Hitachi). The tensile strength was measured by electric tensile tester (TCS-2000, Taiwan) with a speed of 50 mm/min at room temperature. The samples were prepared according to ASTM D-638. The impact tests were measured by charpy impact tester (GT-7045-MDL, Taiwan) according to ISO 180-1.

5.3 Results and discussion

5.3.1 Influence of reaction temperature on production of PDEPDM

The reaction temperature (T) is important in the organic synthesis experiment, the different temperature would lead to the different chemical reaction and product. It could be observed from Fig.5.1, the production increased with the increase of reaction temperature till T increased to 85°C. At low T, chemical reactions take place easily [10], with T increasing, productive capacity of reaction system of PDEPDM increased, because the reaction rate increase with the temperature increasing, and correspond to faster motion of the particles, the chemical reaction went on towards the right, reaction time became shorter, As T increased to 85°C, high heat lost amd chemical reaction was more strong, at the same, the large of HCl would volatile to lead to the pollution [11-12]. And the product would loss water and happen carbonization phenomenon, just as the above reasons, which showed a maximum at 85°C.

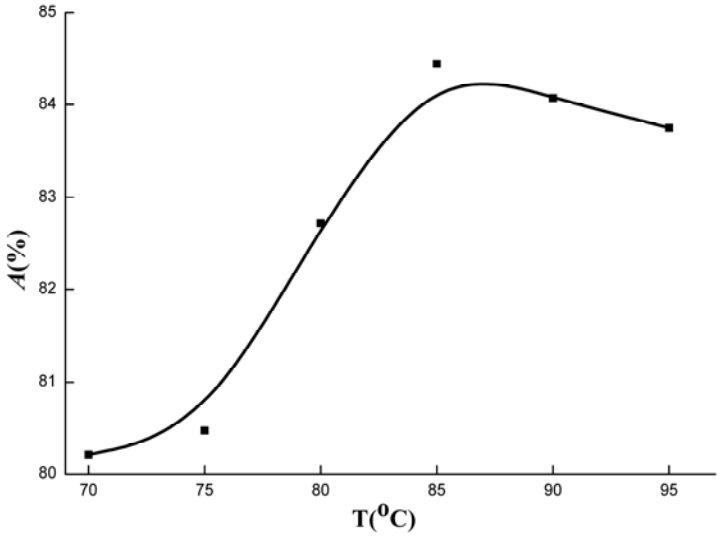


Fig.5.1 influence of reaction temperature on A%

5.3.2 Influence of reaction time on the production of the PDEPDM

Fig.5.2 presented the influence of reaction time (t) on the production (*A*%). It could be found the maximum *A*% arrived at 5 h, and then decreased. As the mention above, when the reaction time was short, the reaction can not react completely, the content of the product was low. In the later treatment, the defect of tedious operation would happen in the experiment, if the reaction time increased [13], the *A*% would remained stable and the reaction reached equilibrium, the reaction time continued to increase, the *A*% would not change, so the optimal time was 5 h.

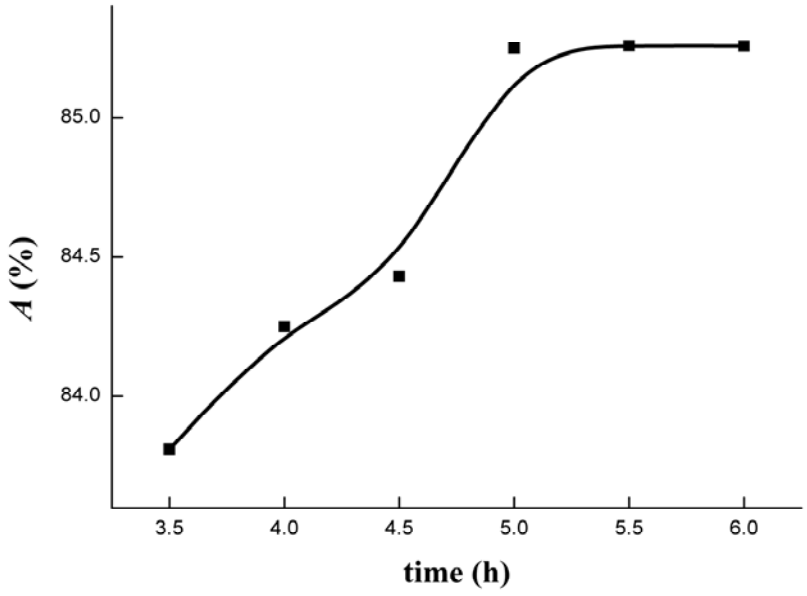


Fig.5.2 Influence of reaction time on A%

5.3.3 FT-IR spectra of PDPPE, PDCEPE and PDEPDM

The FT-IR spectra (KBr pellet) are shown in Fig.5.3. The characteristic infrared absorbed peaks for PDPPE are at 3316 cm^{-1} (-OH), 2813 cm^{-1} (C-H), 1200 cm^{-1} (P-O),

1168 cm^{-1} (P-O-C), respectively. As for PDCEPE, the characteristic infrared absorbed peaks are at 2877 cm^{-1} (C-H), 1169 cm^{-1} (P-O), 929 cm^{-1} (P-O-C), respectively. As for PDEPDM, the characteristic infraredabsorbed peaks are at 1218 cm^{-1} (P-O), 1171 cm^{-1} (P-O-C), and 1663 cm^{-1} (C-N), 3172 cm^{-1} (N-H), respectively. From the analysis, it could be demonstrated that PDEPDM have been prepared, and the intermediate product PDPPE and PDCEPE were successfully synthesized.

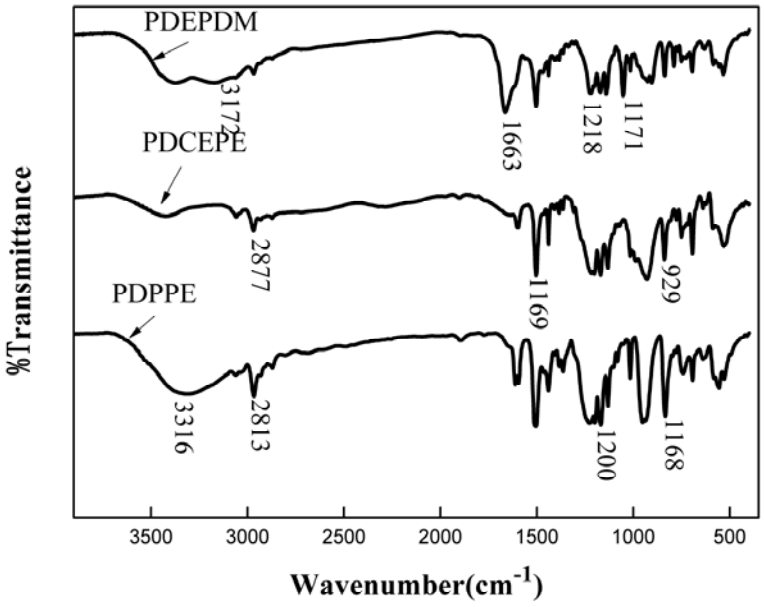


Fig.5.3 The FTIR spectra of PDPPE, PDCEPE and PDEPDM

Similarly, compared with the spectrum of PDCEPE, the crest of absorption peak at 1200 cm^{-1} (P-O) and 1168cm^{-1} (P-O-C) in PDPPE have been red shifted to 1169 cm^{-1} and 929 cm^{-1} in PDCEPE, and the absorption peak of -OH occurred at 3316 cm^{-1} disappeared, which indicates that the structures of PDPPE and PDCEPE are different from each other. However, peaks at 1169 cm^{-1} and 929 cm^{-1} in PDCEPE have been blue shifted to 1218 cm^{-1} and 1171 cm^{-1} in PDEPDM, and Fig.5.3 showed the absorption peak of $-NH_2$ occurred at 3172 cm^{-1} and C-N occurred at 1663 cm^{-1}, all above indicated

PDEPDM was prepared successfully.

5.3.4 NMR analysis of PDPPE, PDCEPE and PDEPDM

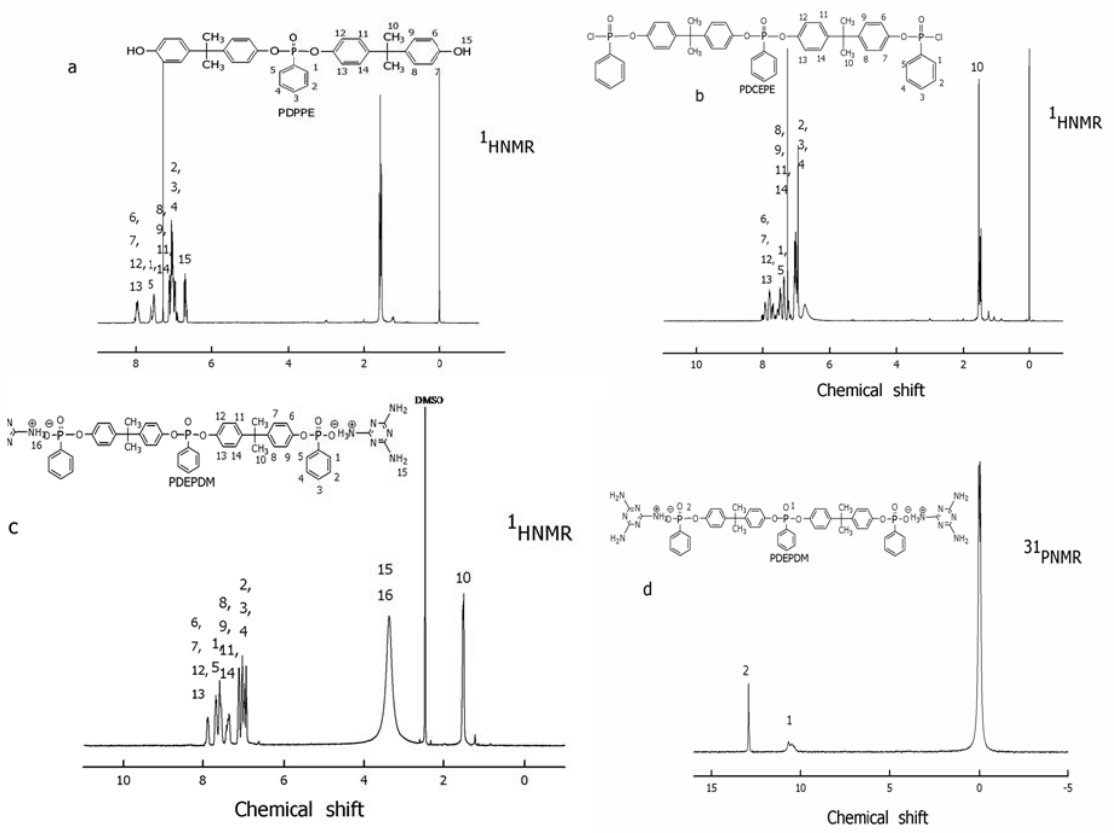


Fig.5.4 The ^{1}HNMR spectrum of PDPPE (a), PDCEPE (b), PDEPDM (c) and the ^{31}PNMR spectrum of PDEPDM (d)

The chemical structures of PDPPE, PDCEPE and PDEPDM were characterized by ^{1}HNMR and ^{31}P NMR, Fig.5.4a-c show the ^{1}HNMR spectra of PDPPE, PDCEPE and PDEPDM, respectively. The NMR spectrum of PDPPE shows some characteristic peaks in Fig.5.4a: the peak at 1.70 ppm is assigned to the protons of =CR-CH_3; the peak of the protons of -OH was 6.86 ppm; the peak at 7.08-8.50 ppm are the protons of Ar-H; After reaction with PPD, the signal of hydroxy proton disappears (-OH 6.86ppm), as

shown in Fig. 5.4b, after the PDCEPE reacted with MA, new signals corresponding to $-NH_2$ and $-NH_3$ appear at 2.29 and 3.36 ppm, as shown in Fig.5.4c. Fig.5.4d presents ^{31}P NMR spectra of the PDEPDM, respectively.

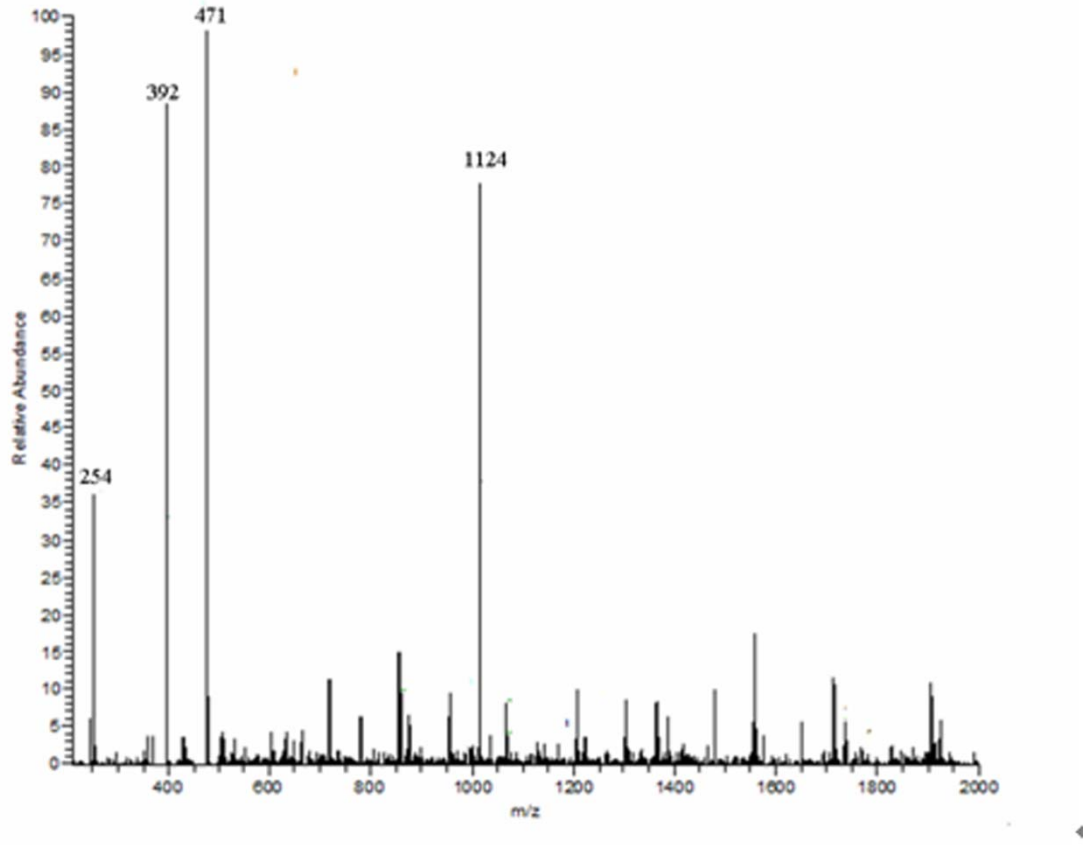
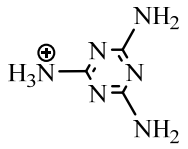
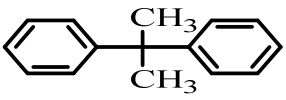
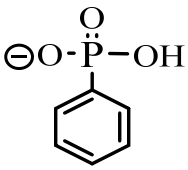


Fig.5.5 ESI-MS of PDEPDM

It can be observed that the PDEPDM spectrum exhibits two single peaks at 13.6 and 11.5 ppm. At the same time, ESI-MS results of PDEPDM showed in Fig.5.5, it can be seen that m/z=1124 corresponds to $C_{55}H_{59}N_{12}O_9P_3$ (PDEPDM), because the PDEPDM included many different repeating unit, which were listed in the Table 5.1. The m/z=471 was the structure of the $C_{18}H_{18}O_9P_3^{3-}$, m/z=392 and 254 corresponds to $C_{30}H_{32}$ and $C_6H_{14}N_{12}^{2+}$. Every m/z value corresponds to the structure of the PDEPDM. These results indicate that PDEPDM was successfully prepared. Therefore, the

proposed structure of PDCEPDM could be confirmed by the FTIR, NMR and ESI-MS, the target product was synthesized.

Table 5.1 Structural assignments in the ESI-MS of PDCEPDM

Structure Unit	m/z	Structure Unit	m/z
	254		392
	471		

5.3.5 Thermal properties

TG and DTG are the most effective technique for characterizing the thermal stability of various polymers.

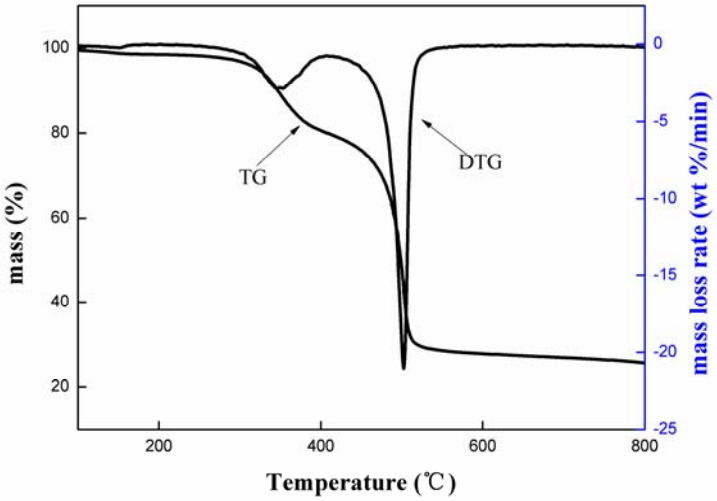


Fig.5.6 The TG and DTG curves of the PDEPDM

Fig.5.6 showes the thermal degradation behaviors of the PDEPDM, the weight loss of the nitrogen-containing structure of the PDEPDM were significantly higher than the other group at 319.8-400°C, the mass loss was 21.09%, and the mass of the one step decomposition temperature was 345.6°C, which shows the nitrogen-containing structure have a lower decomposition temperature, the weight loss of the PDCEPE were significantly low at 400-550°C, the mass loss was 50.25%, and the mass of the two step decomposition temperature was 502.3°C which shows the nitrogen-containing structure have a higher decomposition temperature, when the temperature exceeded 650°C, the mass loss keep stable, the char yields of PDEPDM was 25.29%.

5.3.6 Flame properties of PDEPDM

Table 5.2 LOI Values and UL 94 rating from flame resistance tests for PE/PDEPDM

Samples	Content of PDEPDM (wt %)	LOI	UL-94 rating
PE-1	0	18.0	burning
PE-2	4.0	19.0	burning
PE-3	8.0	20.1	burning
PE-4	16.0	20.9	V-2
PE-5	24.0	22.4	V-2
PE-6	32.0	29.8	V-0
PE-7	40.0	33.8	V-0

To evaluate the flame resistance, PDEPDM was added into polyethylene (PE) by measuring their LOI values [14-15], the LOI of different percentage of PDEPDM in the PE was showed in Table 5.2. With an increase of PDEPDM, the LOI value

increased gradually, when the percentage of the PDEPDM was 32 wt %, the LOI reached 29.8, the results clearly indicate that flame retarded PE composite can be obtained easily by filling new flame retardant PDEPDM. UL 94 test results are also given in Table 5.2. UL 94 V-0 rating was obtained at 32 wt % loading for PE, respectively, which has the exactly same regular as that observed in the LOI experiments discussed before. From these results, it show that PDEPDM is an effective additive-type flame retardant applicable to PE.

5.3.7 SEM analysis of char residue after combustion

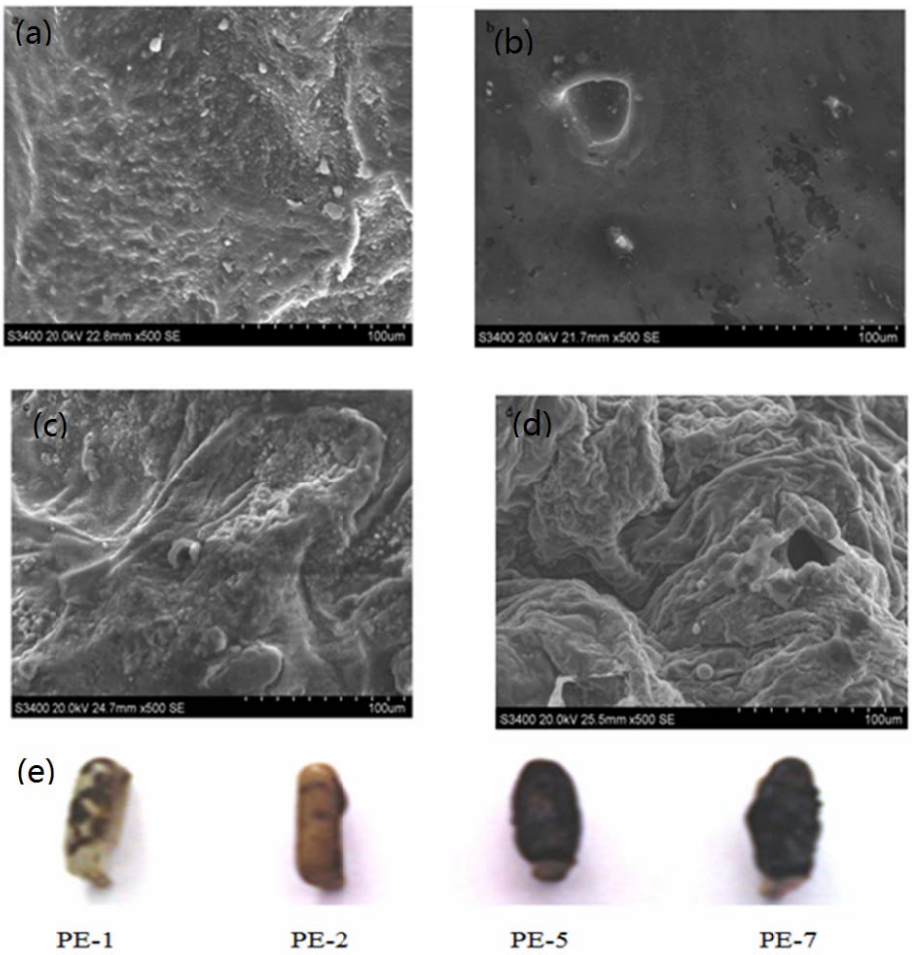


Fig.5.7 SEM photographs of flame retardant PE composites. a PE-1, b PE-2, c PE-5, d PE-7, e the surface morphology of the PE

SEM morphologies in Fig.5.7 also show different char morphology of the PE-1, PE-2, PE-5 and PE-7 composites to be obtained during LOI test. Investigation on the morphology of the char is helpful to explain the differences in the flame retardancy among the flame retardant PE composites. For PE without PDEPDM (Fig.5.7a), the surface of the PE-1 appears to be smooth, flat and no expansion, this structure is beneficial to gas diffusion and heat transfer, which makes the sample burn easily. At the same time, it is not able to swell and form intumescent char layer due to the lack of a carbon source. However, while the surfaces of PE-2(b), PE-5(c) and PE-7(d) show the binding of the chemicals. In the Fig.5.7b could be observed that there were some cracks and hole on the surface of PE-2, compared with PE-1, the surface was coarse, and it could not provide a good flame shield for the material beneath. Because 4% PDEPDM was merely added into the PE, the surface has no enough physical barrier to spread the flammable gases and prevent heat transfer.

However, in Fig.5.7c and d, the surfaces provide the good flame shield for the underlying material by forming a frothy and swollen outer layer and its inner char was fragmental. This protective layer helps keep the material from being destroyed by further burning. The form of the blisters dued to the entrapment of the decomposition gas between the coating of P-N [16-17]. The intumescent charred layer of sample PE-7 (Fig.5.7d) is very compact and much char stacked together seemed to possess bigger thickness and less susceptible to crack, which provides a much better barrier to the transfer of the heat, combustible gases, and free radicals during a fire. So, it can be concluded that when PDEPDM and PE are synergized together at a certain ratio, a high quality of charred layer can be formed. Those results were in accordance with the results of TGA, LOI, and UL 94 testing. The formation of char layer demonstrated that

P-N of PDEPDM played an important role.

5.3.8 Thermal properties of PE-1, PE-5 and PE-7

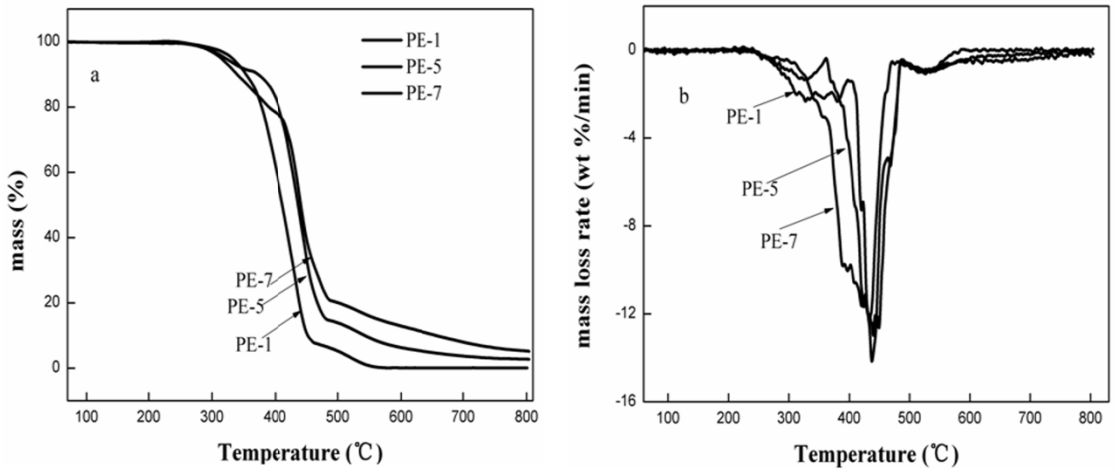


Fig.5.8 TG and DTG curves of the samples under the air atmosphere (a) TG curves of PE-1, PE-5 and PE-7; (b) DTG curves of PE

The thermal stabilities and thermal degradation process of the PE-1, PE-5 and PE-7 were investigated by TGA under air atmosphere. The TGA and DTG curves mainly reflect the stages of the release of decomposition products and the formation of chars. Table 5.3 shows the TGA and DTG values of the PE with different ratios of PDEPDM. Fig.5.8 shows the TGA (8a) and DTG (8b) curve of PE-1, PE-5 and PE-7 under air atmosphere. It showed the onset degradation and maximum decomposition temperatures for PDEPDM/PE systems are slightly lower than neat PE and the weight loss of the PDEPDM/PE at 450-510 ^{o}C were significantly lower than the neat PE, the major reason was the P-N group degrading at a relatively low temperature, the flame retardant PDEPDM containing the P-N functional groups caused the poorer thermal stability for the weak P-O-C bond decomposition at low temperature, with the addition

increase of the PDEPDM, the T_{onet} and T_{max} decreases, and the T_{onet} and T_{max} of PE-1, PE-5 and PE-7 are showed in Table 5.3 respectively, which are much lower than the onet degradation and the max temperature for neat PE. The char yield was 0.08 wt % for neat PE, with the addition increase of the PDEPDM, the char yield reached 2.71 wt% for PE-5 and 5.17 wt% for PE-7 at 800°C. These results in the Table 5.3 suggest that PE has poor thermal stability. With an increase of PDEPDM, the T_{onet} and T_{max} decreased, however the carbon residues increased, so incorporation of PDEPDM can improve the stability of the PDEPDM/PE hybrids at higher temperature and promote the formation of char residue.

Table 5.3 TG Data of the PE-1, PE-5 and PE-7 under air atmosphere

Samples	T_{onet} (^{o}C)	T_{max} (^{o}C)	Mass loss rate at T_{max} (wt%/min)	Residues at 800 °C
PE-1	367.5	506.6	14.24	0.08
PE-5	293.1	486.6	12.85	2.71
PE-7	281.7	476.3	12.04	5.17

5.3.9 Mechanical properties

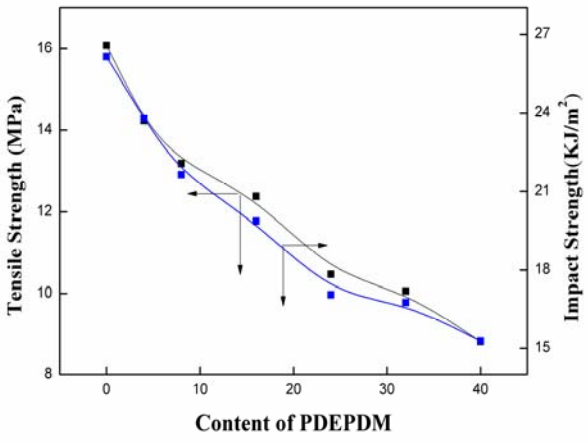


Fig.5.9 Mechanical properties of composites

The mechanical properties of the PE/PDEPDM were characterized by vertical drawing test and cantilever impact test. The results were shown in Table 5.4 and Fig.5.9.

Table 5.4 Mechanical properties of the PE/PDEPDM

Samples	Content of PDEPDM (wt %)	Tensile Strength (MPa)	Impact Strength (kJ/m^2)
PE-1	0	16.08	26.14
PE-2	4.0	14.23	23.79
PE-3	8.0	13.19	21.65
PE-4	16.0	12.38	19.87
PE-5	24.0	10.47	17.06
PE-6	32.0	10.06	16.77
PE-7	40.0	8.81	15.28

With the increase of PDEPDM, the flame-retarded PE presented lower tensile and impact strengths than PE. Compared with PE, the mechanical properties of flame-retarded samples gradually decreased with an increase dosage of PDEPDM. Tensile strength and impact strength of the PE were 16.08 MPa and 26.14 kJ/m^2, However, when the PDEPDM was added into the PE, the corresponding strength values decreased, when the 40% PDEPDM was filled, the tensile strength and impact strength were 8.81 MPa and 15.28 kJ/m^2, the tensile strength falled 45.21%, and impact strength dropped 41.54% than the PE-1 respectively. The mainly reason for the mechanical strength decreasing was just for the excessive filling of PDEPDM, because the PDEPDM has P-N molecular structure, when the flame retardant was filled into the PE, the steric effect led to the cross-linking density of PE decrease, which deteriorate the mechanical properties of flame-retarded PE [18]. The conclusion can be drawn that the reactive flame retardant PDEPDM improved the flame resistance of PE, while the mechanical properties had a decrease. In order to consider the combination properties of flame-retarded PE, the sample of PE-6 has the best performance, tensile strength and impact strength were 10.06 MPa and 16.77 kJ/m^2.

5.4 Conclusions

The research demonstrated PDEPDM flame retardantwas prepared successfully by three step reactions, and the PDEPDM was charactered by the FTIR, NMR and TG. In order to obtain high purity of the PDEPDM, the suitable reaction conditions needed to be controlled, such as reaction temperature, reaction time and solvent ratio, fabrication conditions were optimized, shown as the follows: reaction temperature was 85^{o}C, reaction time was 5 h and the solvent ratio of the n_{MA}:n_{PDCEPE} was 2.1:1, it was

also studied the flame performance, the PDEPDM was added into the polypropylene, and the performance of the flame retardant was researched by LOI and UL 94 rating. When the 32% PDEPDM was filled, the flame properties can reach V-0 rating and the tensile strength and impact strength were 10.06 MPa and 16.77 kJ/m^2.

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Chapter 6

Synthesis of intumescent flame retardant PMXSPB and its application in epoxy resin

6.1 Introduction

Epoxy resin (EP) is a very important thermosetting polymer because of its superior electrical and mechanical properties, excellent adhesion to many substrates, low curing shrinkage, and excellent resistance to moisture, solvents, and chemical agents. It is used as a high-performance material in various applications, such as adhesives, coatings, laminating packing, electronic/electrical insulation, and composites [1]. However, pure EP resin is highly inflammable, which significantly limits its applications. Therefore, the modification of EP resin to improve its flame resistance is an important research topic [2]. Compared with the preparation of intrinsic flame-retarded EP resin, the synthesis of special hardeners that contain flame-retardant functional groups has many advantages, including simplicity and easy controllability, and these advantages have resulted in progress toward the fabrication of flame-retarded EP resin composites with excellent combination properties. The frequency of literature reports on reactive curing agents containing phosphorus has been increasing in recent years [3]. Isara Jirasutsakul et al. synthesized two novel aromaticamine curing agents containing phosphorus and incorporated them into EP resins, achieving limiting oxygen index (LOI) values of 27 and 31 in phenyl phosphonic ethylenediamine diamide-cured EP resin and phenyl phosphonicp-phenylene diamine diamide-cured EP resin, respectively, for comparison, the LOI values of resins prepared without phosphorus curing agents were 20 for ethylenediamine and 21 for propylenediamine [4]. Lv et al.

synthesized a novel poly-(melamine-ethoxyphosphinyl-diisocyanate) (PMPC) for use in EP resins, and the LOI value of EP/PMPC-containing 20 wt% PMPC reached 28.0 with a UL 94 V-0 rating. A 9, 10-dihydro-9-oxa-10-phosphaphenanthrene 10-oxide-containing flame retardant for EP resins was previously synthesized by our group, which provided excellent combination properties, including an LOI value of 35.5 and the vertical burning test reaching the UL 94 V-0 rating [3, 5-7]. Several novel flame-retardant curing agents have been synthesized by Agrawal and Narula [8], Durga and Narula,[9] Zhan et al.,[10] Braun et al.,[11] and Perezet al.,[12] and their EP resins showed attractive combined properties, with LOI values as high as 39.9 and the vertical burning test reaching the UL 94 V-0 rating. In comparison with amine curing agents, an acid anhydride curing agent offers several advantages, including lower volatility, lower toxicity, and a longer usage time, and the resulting cured resin exhibits excellent electrical properties and smaller volumetric shrinkage.

In this chapter, a novel flame retardant curing agent containing phosphorus and nitrogen (N), poly-(meta-xylylenediaminespirocyclic pentaerythritol bisphosphonate) (PMXSPB), was synthesized. A series of flame-retarded EP resin composites were prepared by filling PMXSPB with different fractions, and the flame resistance, thermal properties, and mechanical properties of the flame retarded composites were investigated in detail.

6.2 Experiment

6.2.1 Materials

All of the starting materials and solvents were commercially available and were used without further purification. Pentaerythritol (PER), acetonitrile, and

dichloromethane (CH_2Cl_2; analytical reagent) were purchased from Sinopharm Chemical Reagent (Liaoning, China). Phosphorus oxychloride ($POCl_3$, AR) and m-xylylenediamine (MXDA, chemically pure) were purchased from Beijing Lideshi Chemical Co. Ltd (China). Methylhexa hydrophthalicanhydride (MeHHPA, hardener) was purchased from dianhydride 1,4-bis(phthalic anhydride-4-carbonyl)-2-(6-oxido-6H-dibenz [c, e][1,2]-oxaphosphorin-6-yl)-phenyleneester (BPAODOPE) was synthesized by our group. The EP resin (bisphenol A diglycidyl ether, trade name E-51, EP equivalent = 180-196 g/eq) and the EP reactive diluent aliphatic glycidyl ether (AGE) were purchased from the Wuxi Resin Factory (Jiangsu, China). The other reagents were used as received from commercial sources or purified by standard methods.

6.2.2 Synthesis of SPDPC

First, 54.46 g of PER (0.4 mol), 96.9 ml of $POCl_3$ (1.04 mol), 200 ml of chlorobenzene, and 1 g of aluminumchloride (catalyst) were mixed in a 500 ml glass flask equipped with a condenser, a N_2 inlet, a thermometer, a magnetic stirring bar, and a gas absorber. The mixture was stirred at 60°C for 2 h; then, the reaction temperature was elevated to 100°C, and the reaction was protected with N_2 gas until no hydrogen chloride (HCl) gas was emitted. The chemical reaction process is shownin Fig.6.1. The product was filtered and purified with CH_2Cl_2 and ethanol sequentially and then dried to a constant weight at 80°C under vacuum. A white solid powder was obtained (yield: 80%) [13-20].

6.2.3 Synthesis of PMXSPB

Spirocyclic pentaerythritol bisphosphorate disphosphorylchloride (SPDPC; 59.4

g, 0.2 mol) powders were dispersed in 250 ml of acetonitrile and transferred to a glass flask. MXDA (52.8 ml, 0.4 mol) and acetonitrile (30 ml) were dropped in using a pressure-equalizing dropping funnel. The mixture was continuously stirred at 80°C under N_2 protection. The reaction was completed after 6 h when no HCl gas was detected. The product was filtered and purified by ethanol and then dried to a constant weight at 80°C under vacuum. White solid PMXSPB powder was finally obtained (yield: 97%).

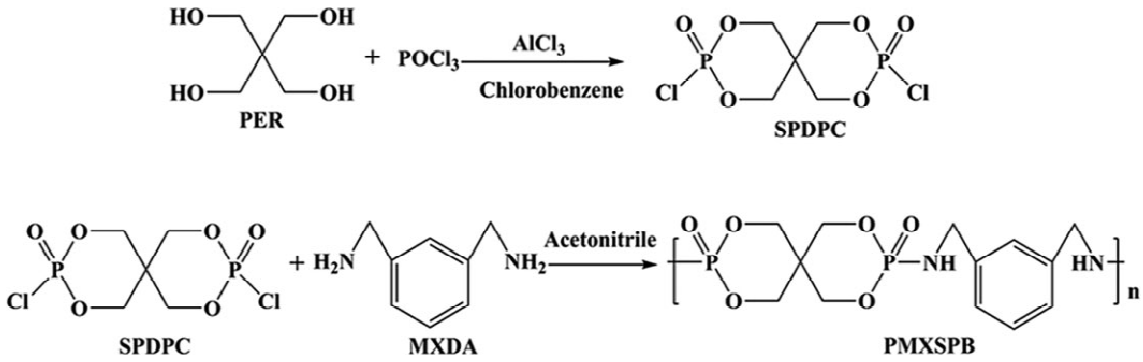

Fig.6.1 Synthesis route of PMXSPB. PMXSPB: poly-(meta-xylylenediamine spirocyclic pentaerythritol bisphosphonate)

6.2.4 Preparation of flame-retardant EP composites

For comparison with the newly synthesized PMXSPB, MXDA was used as a curing agent for pure EP. The BPAODOPE and MeHHPA systems [3] were selected as the curing agent and flame retardant, respectively, for preparing flame-retarded EP composites. The curing conditions for different EP composites were identical. The PMXSPB wasadded to EP resins in different fractions (Table 6.1) and mixed for 10 min at 120°C. The mixture was stirred continuously and placed into an oven at 120°C for 40 min, followed by degassing for 1 h at 80°C under vacuum. Finally, the mixture was

poured into Telflon molds at 130°C. The samples were cured for 2 h at 136°C and then post-cured for 4 h at 150°C.

Table 6.1 Recipes of flame-retarded samples with different contents of PMXSPB

Sample	P (%)	DGEBA (g)	PMX-SPB (g)	MXDA (g)	AGE (g)	BPAO DOPE(g)	MeHHPA (g)
EP-0	0	100	/	20	/	/	/
EP-1	2.67	100	30	/	10	/	/
EP-2	3.01	100	35	/	10	/	/
EP-3	3.32	100	40	/	10	/	/
EP-B	1.75	100	/	/	/	86.4	41.7

PMXSPB: poly-(meta-xylylenediamine spirocyclic pentaerythritol bisphosphonate); P: phosphorus; DGEBA: bisphenol A diglycidyl ether; MXDA:m-xylylenediamine; BPAODOPE: aryl phosphinate dianhydride 1,4-bis(phthalic anhydride-4-carbonyl)-2-(6-oxido-6H-dibenz[c, e][1,2]-oxaphosphorin-6-yl)-phenylene ester; MeHHPA: methylhexahydrophthalic anhydride; EP: epoxy. Calculated by formula : P%= (weight of PMXSPB/total weight of the system)×12.48 wt%×100%, (12.48% is the phosphorus content PMXSPB); Calculated by formula: P% = (weight of BPAODOPE/total weight of the system) ×4.61 wt%×100%. EP-B was synthesized in our group and also employed as cross-linking agent for EP resin as references in order to compare the properties of the phosphorus-containing cross-linking agents with the known system [3].

6.2.5 Characterization

Structure characterization of PMXSPB. Fourier transform infrared (FTIR) spectroscopy was performed on a ThermoNicolet NEXUS-470 (Ramsey, Minnesota,

USA) spectrometer using potassium bromide pellet technique. Protonnuclear magnetic resonance (^{1}H NMR) spectra wererecorded on an AVANCE III 500 MHz spectrometer (Bruker, Switzerland) using deuterated dimethyl sulfoxide (DMSO-d6) as the solvent. The molecular weight ofPMXSPB was determined by mass spectrometry using a Thermo Finnigan LCQ Deca XP (Somerset San Diego, California, USA), with the sample dissolved in DMSO. TG analysis: thermogravimetric analysis (TGA) and differentialscanning calorimetry (DSC) were performed on a STA449C/41G thermal analyzer (NETZSCH, Germany) at a heating rate of 10°C/min in air atmosphere. The weights of the samples were approximately 10 mg.

Flame resistance. The vertical burning tests (UL 94) were measured using a CZF-3 instrument (Jiangning Analytical Instrument Factory, Nanjing, China), and according to the ASTM D3801 testing procedure, the sample dimensions were 130× 13.0×3.0 mm^3. The LOI was measured using a JF-3 LOI chamber (Jiangning Analytical Instrument Factory), and according to the ASTM D2863 standard, the sample dimensions were 130×6.5×3.0 mm^3. The percentage of oxygen (O_2) in the O_2/N_2 mixture was taken as the LOI that was just sufficient to sustain the flame.

Microstructure. Scanning electron microscopy (SEM) using an S-3400N instrument (Hitachi, Japan) was used to investigate the combustion residues of burned samples from vertical burning tests.

Mechanical property tests. The tensile strength tests of 4.0-mm-thick samples were performed according to the International Organization for Standardization (ISO 527-2 standards using a TCS-2000 electric tensile tester (Gotech testing machines Inc., Taiwan), and the tests were performed at a speed of 5 mm/min at room temperature. All of the listed results are the mean of five samples. Charpy impacttests were performed

according to ISO 179-1 standard using a GT-7045-MDL Charpy impact tester (Taiwan).

6.3 Results and discussion

6.3.1 Composition and thermal properties of PMXSPB

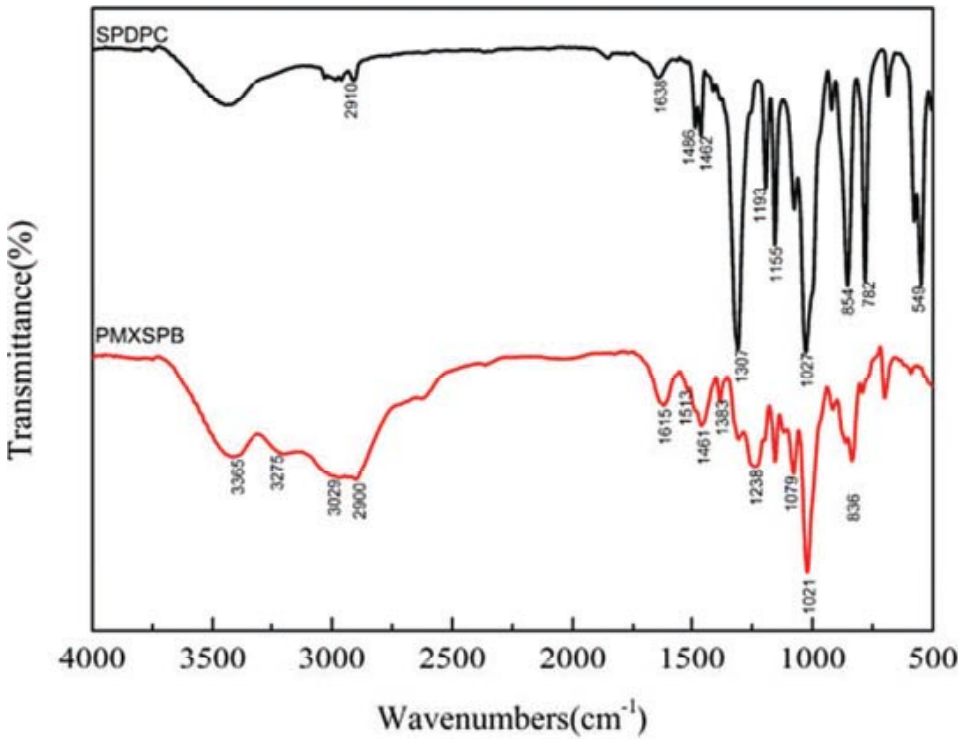

Fig.6.2 FTIR spectra of SPDPC and PMXSPB. FTIR: Fouriertransform infrared spectrometry; SPDPC: spirocyclic pentaerythritolbisphosphorate disphosphoryl chloride; PMXSPB: poly-(meta-xylylenediamine spirocyclic pentaerythritolbisphosphonate).

Fig.6.2 shows FTIR spectra of SPDPC and PMXSPB. There are several absorption peaks for SPDPC: 1027 cm^{-1} (P-O-C), 854 cm^{-1} (P-O), 1307 cm^{-1} (P=O), and 549 cm^{-1} (P-Cl), in agreement with the previous report [17]. Inthe FTIR spectra of PMXSPB, absorption peaks areobserved at 3365, 3275, 1615 cm^{-1} ($-NH_2$), 3029 cm^{-1} (C-H), 1513 cm^{-1} (C=C), 1238 cm^{-1} (P=O), 1021 cm^{-1} (P-O-C), and 1079 cm^{-1} (P-N). The disappearance of the peak at 549 cm^{-1} (P-Cl) indicates the completion of the

chemical reaction in Fig.6.1.

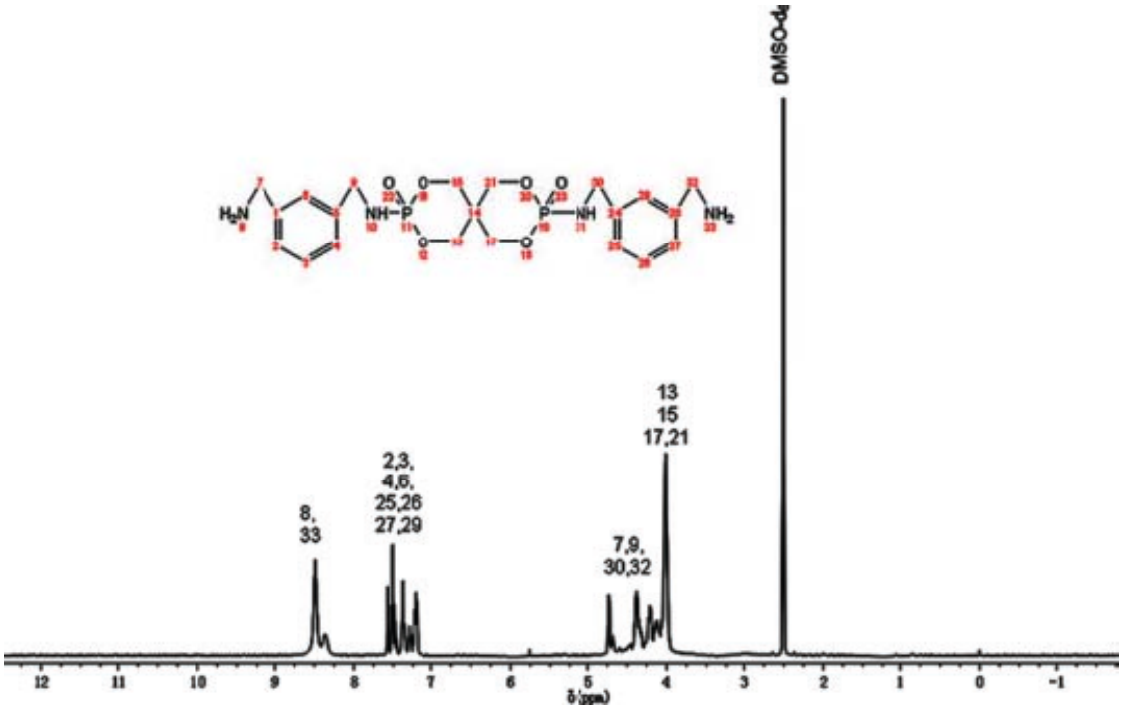

Fig.6.3 ^{1}H NMR spectrum of PMXSPB (500 MHz, DMSO-d6).^{1}H NMR: proton nuclear magnetic resonance; PMXSPB: poly-(meta-xylylenediamine spirocyclic pentaerythritol bisphosphonate); DMSO-d6: deuterated dimethyl sulfoxide.

In addition to the FTIR spectra, Fig.6.3 shows the ^{1}H NMR spectra of PMXSPB. ^{1}HNMR (500 MHz, DMSO-d6) δ 8.49 (s, 4H), 8.36 (s, 2H),7.57 (s, 1H), 7.54-7.44 (m, 4H), 7.38 (s, 2H), 7.43-7.26(m, 2H), 7.25-7.18 (m, 3H), 4.70 (dd, J=26.7, 6.3 Hz,2H), 4.42-4.29 (m, 5H), 4.20 (d, J = 6.1 Hz, 1H), 4.01(dt, J = 9.8, 5.5 Hz, 8H). The m/z values 496, 856, and 1217 in the mass spectrum in Fig.6.4 correspond to MH^{+}, M_2H^{+}, and M_3H^{+}, respectively, where M is the repeating unit of PMXSPB. The structure of PMXSPB was confirmed by FTIR, ^{1}H NMR, and mass spectrum, and all of the results confirmed that the target product was synthesized successfully as shown in Fig.6.1.

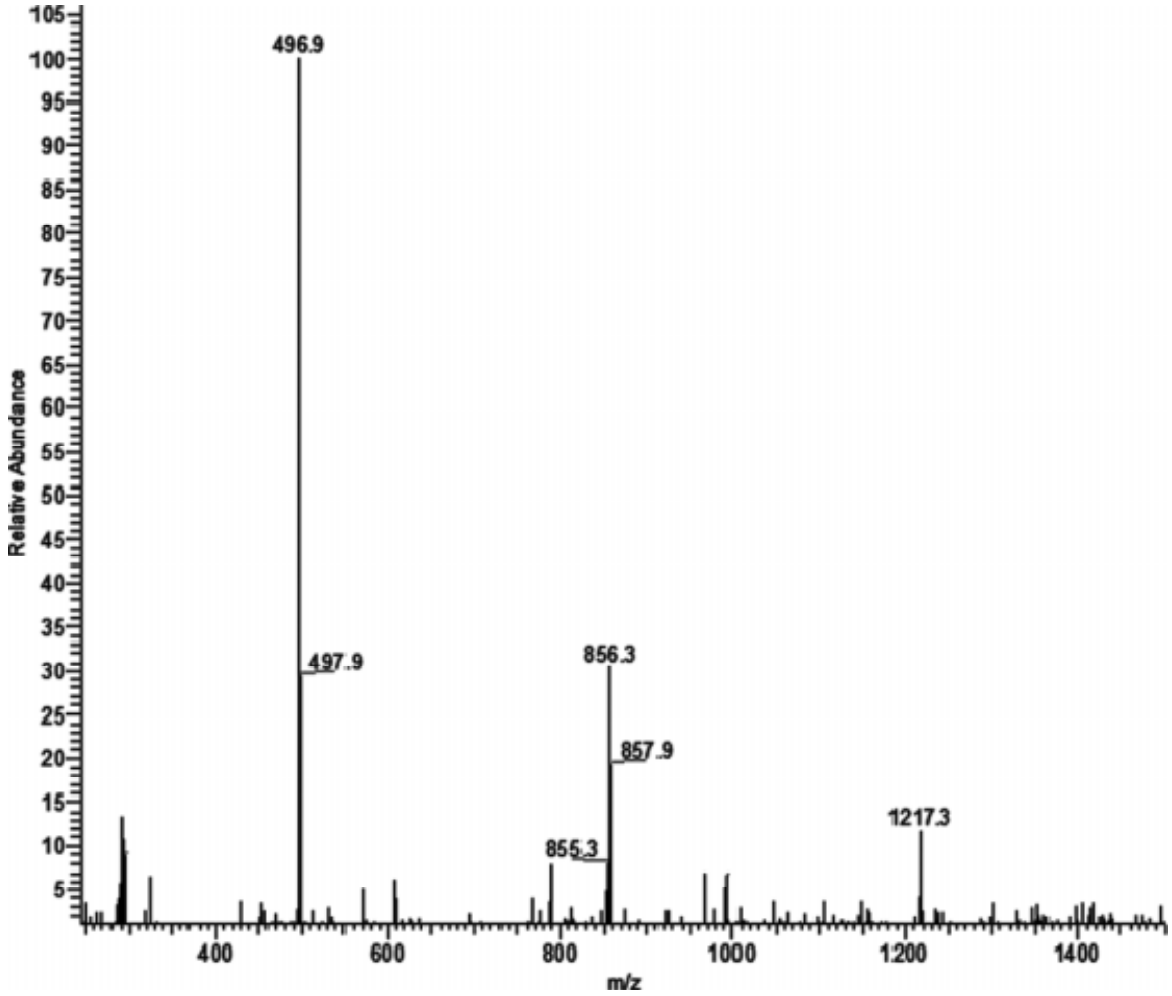

Fig.6.4 Mass spectrum of PMXSPB. PMXSPB: poly-(metaxylylenediaminespirocyclic pentaerythritol bisphosphonate)

Fig.6.5 shows the TG and differential thermogravimetric (DTG) curves of PMXSPB. The TGA results show that PMXSPB starts to decompose at 306°C and that the mass of the residue is 50.6% of the initial mass at 600°C in air atmosphere. The higher char weight indicates that PMXSPB is an efficient char-forming agent. The DTG results indicate that PMXSPB undergoes a major weight loss of 12.5% at 320°C, which is attributed to the fracture of the phosphate ester bonds [17]. The higher decomposition temperature of PMXSPB can satisfy the processing requirements of commonly used polymers.

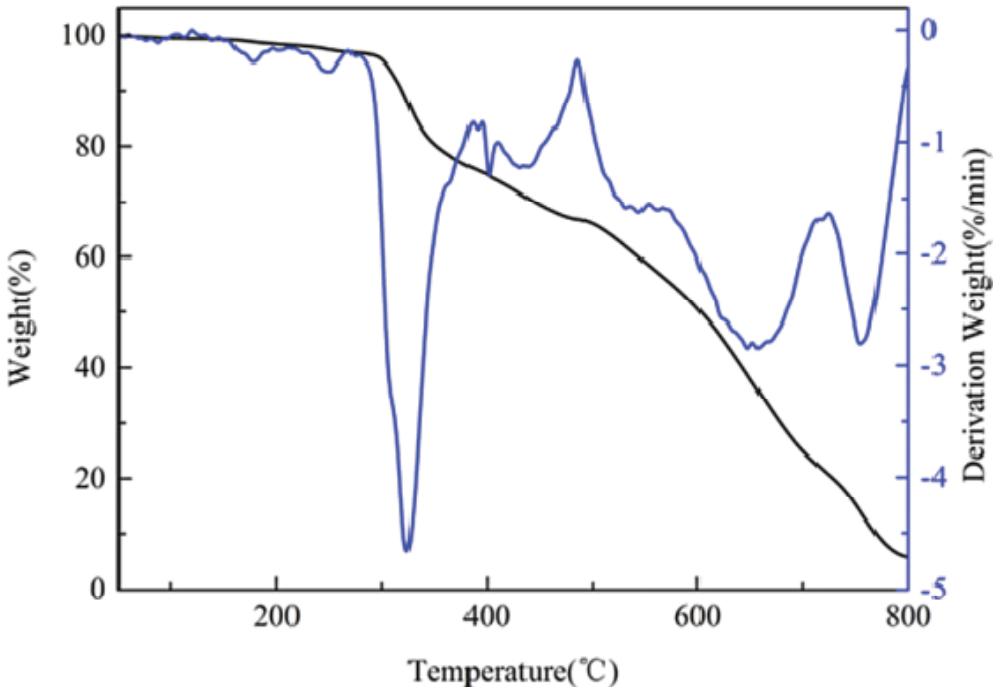

Fig.6.5 TG and DTG curves of PMXSPB in air atmosphere. TG: thermogravimetric; DTG: differential thermogravimetric; PMXSPB: poly-(meta-xylylenediamine spirocyclic pentaerythritol bisphosphonate).

6.3.2 Thermal curing behaviors and curing kinetics of EP/PMXSPB composite

The curing behaviors of the thermosetting systems consisting of EP resin and flame-retardant curing agent PMXSPB were investigated using dynamic DSC. Different heating rates were set for EP/PMXSPB (EP 100 g and PMXSPB35 g) samples as shown in Fig.6.6. The curing reaction of the halogen-free flame-retardant system was an exothermic reaction with a wide temperature range. Meanwhile, the initial curing temperature (T_i), exothermic peak temperature (T_p), and terminated curing temperature (T_e) were directly obtained from the curves in Fig.6.6.

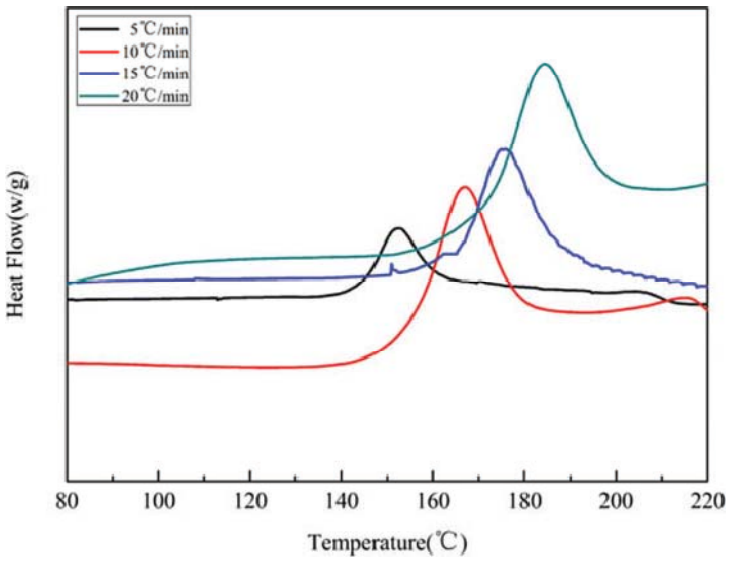

Fig.6.6 DSC curves of different EP/PMXSPB composites curing at various heating rates. DSC: differential scanning calorimetry; EP: epoxy; PMXSPB: poly-(meta-xylylenediamine spirocyclicpentaerythritol bisphosphonate).

The T_p shifted to higher temperatures with an increase in the scanning rate, which has also been previously described in the literature [21]. The relationships between heating rate β and T_i, T_p, and T_e are plotted in Fig.6.7.

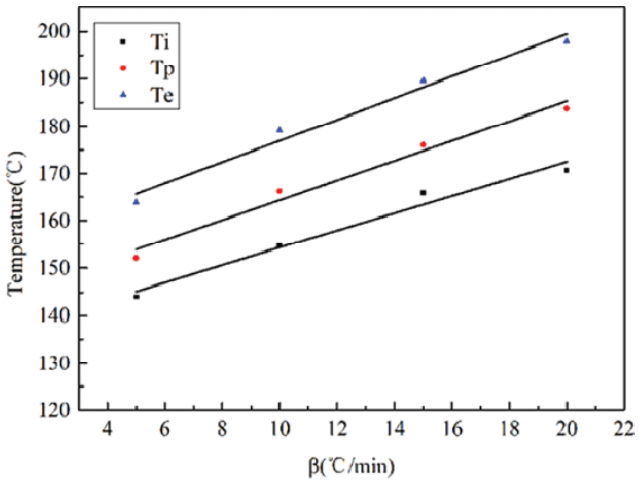

Fig.6.7 The curing temperature curves of EP/PMXSPB with different heating rates. EP: epoxy; PMXSPB: poly-(meta-xylylenediaminespirocyclic pentaerythritol bisphosphonate.

The gel temperature of the system was obtained by extrapolation to β= 0, and the curing temperature and the post treatment temperature can be calculated as follows: T_{gel}= 136°C, T_{curing}= 143°C, and $T_{posttreatment}$= 155°C. Thus, the selected curing conditions for the EP/PMXSPB composite were a pre-curing treatment for 4 h at 136°C and a subsequent curing treatment for another 6 h at 150°C. Because of the poor dispersion of flame retardant curing agent particles in the EP matrix, the curing conditions would be different when certain powders are incorporated into EP resins. To determine the dose of curing agent, the cured products were characterized by FTIR to obtainthe best recipe. As shown in Fig.6.8, the EP group characteristic adsorption peak at 913 cm^{-1} appears when the PMXSPB content is 25 g, and the peak intensity decreases when the PMXSPB content is 30 g, and disappears when the PMXSPB is further increased to 35 g and 40 g. Therefore, the best curing recipe for PMXSPB is 100 g EP resin to 30 g PMXSPB.

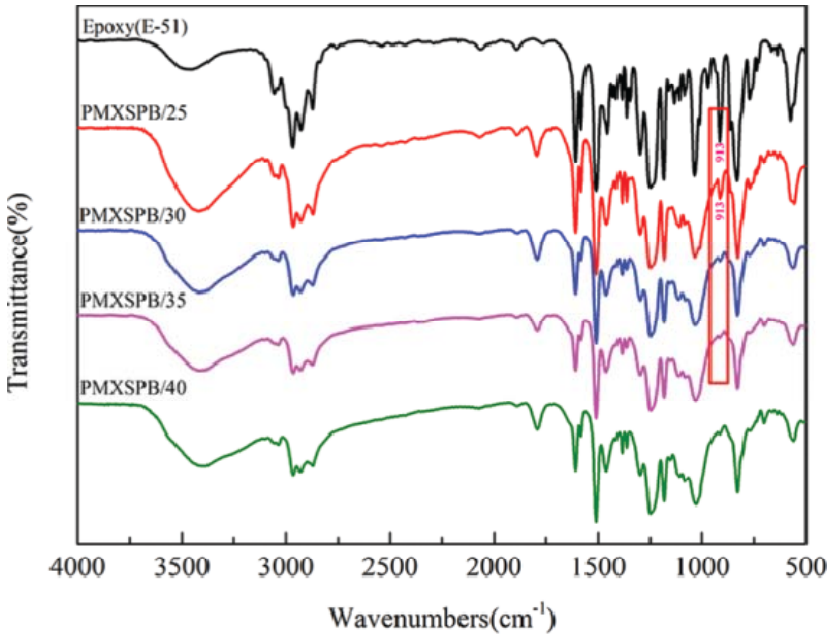

Fig.6.8 FTIR spectrum of EP/PMXSPB composites with different contents of PMXSPB.

6.3.3 Thermal stability of EP/PMXSPB composites

The characteristic values of the TG curves in Fig.6.9 a are listed in Table 6.2.

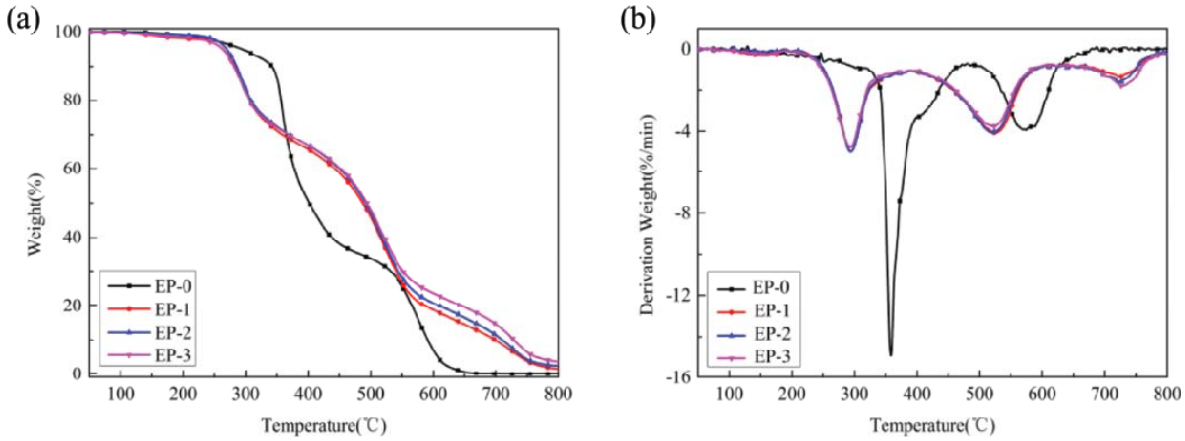

Fig.6.9 TG (a) and DTG (b) curves of EP/PMXSPB composites with different contents of PMXSPB in air atmosphere. TG: thermogravimetric; DTG: differential thermogravimetric; EP: epoxy; PMXSPB: poly-(meta-xylylenediamine spirocyclic pentaerythritol bisphosphonate).

The onset degradation temperatures of the EP/PMXSPB systems are slightly lower than those for pure EP, which shows that the phosphorus-containing EP resin composites have a lower decomposition temperature. A possible reason is the phosphorus group degradation at a relatively low temperature between 220°C and 280°C, where the network's backbone of cured EP-containing phosphorus functional groups causes diminished thermal stability because of the weak P-O-C bond decomposition at low temperatures.[3,22] These results are consistent with those reported for other phosphorus-containing EP resins.[3,15] The residual char ratios of the EP/PMXSB composites are significantly higher than the ratio for pure EP, between 370°C and 530°C, which demonstrates that PMXSPB can retard the decomposition of the composite through the decomposition of P-O-C bonds. The main reason for this

retarded decomposition is that degradation of the flame retardant will promote the formation of charlayers, which cover the surface of the burning substance and reduce the decomposition rate of the EP matrix, thus preventing burning of the composites. As shown in Table 6.2, the residual char ratio increases remarkably with increasing phosphorus content. Under the same conditions, the residue fraction of pure EP is 6.9% at 600°C, whereas in the case of flame-retarded EP resin with 3.32% phosphorus, the residue is 23.6%. These results demonstrate that the addition of the new flame-retardant PMXSPB decreases the onset decomposition temperature of the composite but also retards the decomposition rate of the composite by increasing the residual char ratio. The glass transition temperature (T_g) of the cured EP resins was measured using DSC. When the temperature is higher than T_g, the molecular chains of the cured EP resin undergo significant motion. Fig.6.10 shows the DSC thermograms of the cured EP resins, and the Tg values of different samples are listed in Table 6.2. The T_g of pure EP is 129°C, whereas the values for the cured systems with different PMXSPB contents range from 143°C to 150°C. The T_g values of the composites containing PMXSPB are significantly higher than those of the pure EP resin, and the Tg of the composites increases significantly when more PMXSPB is introduced; this behavior is attributable, primarily to the remarkable increase in cross-linking density and to the oxirane-opening reaction of the PMXSPB structure.

Table 6.2 Thermogravimetric properties of cured epoxy resins with different P contents

Sample	P (%)	T_g (°C)	Temperature of weight loss (°C)			Residue (%)	
			T_{onset}	$T_{10\%}$	T_{max}	600	800
EP-0	0	129	293	342	359	6.9	0
EP-1	2.67	143	268	287	524	18.7	2.5
EP-2	3.01	147	269	286	521	20.8	3.4
EP-3	3.32	150	267	282	522	23.6	3.6

P: phosphorus; Tg: glass transition temperature; EP: epoxy.

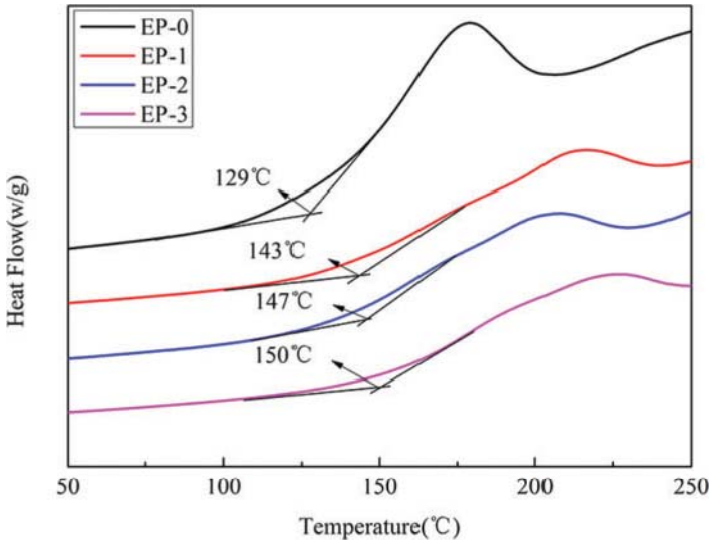

Fig.6.10 DSC curves of EP/PMXSPB composites with a heatingrate of 10°C/min. DSC: differential scanning calorimetry; EP: epoxy; PMXSPB: poly-(meta-xylylenediamine spirocyclic pentaerythritol bisphosphonate).

6.3.4 Mechanical properties and flame resistance of EP/PMXSPB composite

The mechanical properties and flame resistance of different composites were characterized on the basis of the results of tensile tests, charpy impact tests, vertical burning test, and LOI, as listed in Table 6.3. The flame-retarded EP resin with

PMXSPB exhibits lower tensile and impact strengths than pure EP resin. When the phosphorus content is 3.01%, the tensile and impact strengths of the flame-retarded sample EP-2 decrease to 51 MPa and 4.8 kJ/m^2 from 68 MPa and 6.5 kJ/m^2 for pure EP resin, respectively. The main reason for the diminished mechanical strength is the poor dispersion of PMXSPB in the EP resin matrix. Furthermore, PMXSPB has a rigid molecular structure with higher phosphorus and N_2 contents. The rigid structure produces steric hindrance, which decreases the cross-linking density of EP resin; therefore, the mechanical properties of the flame retarded EP resin undergo clear deterioration. The LOI denotes the minimum O_2 concentration required to support flame combustion, which is often used as an indicator to evaluate the flame resistance of polymers. The LOI values of all of the samples are listed in Table 6.3. The LOI values gradually increase from 19.8 to 32.9 as the phosphorus content increases from 0 to 3.32 wt%, which indicates that the flame-retardant curing agent PMXSPB significantly improves the flame resistance of EP resin. The vertical burning test (UL 94) is often used to test the upward burning characteristics of polymers. The result shows that the flame resistance of the cured EP resins increases with increasing phosphorus content, and a UL94 V-0 rating is obtained when the phosphorus content exceeds more than 3.01 wt%. The property of vertical burning further indicates the superior self-extinguishing character of the novel flame-retardant PMXSPB. Given the various properties offlame-retarded EP resin, sample EP-2 which contains 3.01 wt% phosphorus exhibits the best performance witha tensile strength of 51 MPa, an impact strength of 4.8 kJ/m^2, an LOI value of 31.2, and a UL94 V-0 rating. To verify the superior flame resistance of PMXSPB, sample EP-B was prepared with BPAODOPE, which is a novel flame-retardant and curing agent containing phosphorus that we synthesized in our

previous work. The specific recipe for EP-B is listed in Table 6.1, and the properties are given in Table 6.3. First, because the phosphorus content per unit mass of PMXSPB is more than four times greater than that per mass of BPAODOPE, the higher loading of BPAODOPE will degrade the mechanical properties to achieve the final flame resistance. The tensile and impact strengths of EP-B are 31 MPa and 3.5 kJ/m^2, respectively, whereas the tensile and impact strengths of EP-2 are51 MPa and 4.8 kJ/m^2, respectively, indicating the superiority of PMXSPB. Furthermore, the ratio between the flame-retardant PMXSPB and the assistant curing agent AGE is 35/10, whereas the BPAODOPE/MeHHPA ratio is 86.4/41.7, and this difference indicates that PMXSPB not only acts as a flame retardant but can also be used as acuring agent, thus requiring a smaller amount of the assistant curing agent AGE. In addition to the higher flame retardant efficiency and lower filling fraction of PMXSPB, the cost of raw materials is lower and the synthesis processis very simple. As a novel reactive flame retardant and curing agent, PMXSPB has the potential to be industrialized inthe near future.

Table 6.3 Mechanical and flame resistance of the epoxy resins with different flame retardants.

Sample	P (%)	Tensile strength (MPa)	Impact strength (kJ/cm^2)	LOI (%)	UL 94
EP-0	0	68	6.5	19.8	Failed
EP-1	2.67	45	3.5	27.8	V-1
EP-2	3.01	51	4.8	31.2	V-0
EP-3	3.32	44	3.7	32.9	V-0
EP-B	1.75	31	3.5	29.3	V-0

P: phosphorus; LOI: limiting oxygen index; EP: epoxy.

6.3.5 Residue morphologies and flame resistance mechanism

The microstructure of the char residues after combustion was investigated using SEM. The morphologies of the char residues are shown in Fig.6.11. After the pure EP burned, as shown in Fig.6.11a, the surface was very rough, with no dense char layer. In the case of the EP-B sample containing BPAODOPE synthesized in our previous work,[3] compact intact char layers were formed on the residue surface, as shown in Fig.6.11b, effectively preventing the combustion of EP resins. However, in the case of sample filled with PMXSPB, many bubbles formed on the surface of the char layer, as shown in Fig.6.11(c and d), which results in loose porous surfaces in the carbon residue. The special surface further confirms the intumescent flame retardant behavior of PMXSPB.[23] Compared with sample EP-3 (Fig.6.11c), which has a lower phosphorus content of 3.01%, sample EP-4 (Fig.6.11d), which has a higher phosphorus fraction, exhibits far more numerous and larger bubbles in the dense carbon layer. We attempt to illustrate the flame resistance mechanism for the flame-retarded EP with the phosphorus and N-containing flame-retardant PMXSPB. Elemental phosphorus converted into phosphoric acid during combustion, and the further thermal decomposition of phosphoric acid leads to the formation of polyphosphoric acid, and this acid can esterify and dehydrate the pyrolyzing EP polymers and simultaneously produce phosphorus-rich char layers, further inhibiting the pyrolysis reactions of the polymer. The protective layers restrict heat transmission and provide a good flame shield for the underlying material during combustion. In addition, the N_2 in PMXSPB changes into nonflammable gases such as ammonia and N_2, which dilute the O_2 concentration of the combustion surface, demonstrating the important role of PMXSPB in self-extinguishing

flameretarded EP composites [24]. These results indicate that the synthesized flame-retardant and curing agent PMXSPB plays an effective role in promoting residual char and self-extinguishing via an intumescent flame resistance mechanism.

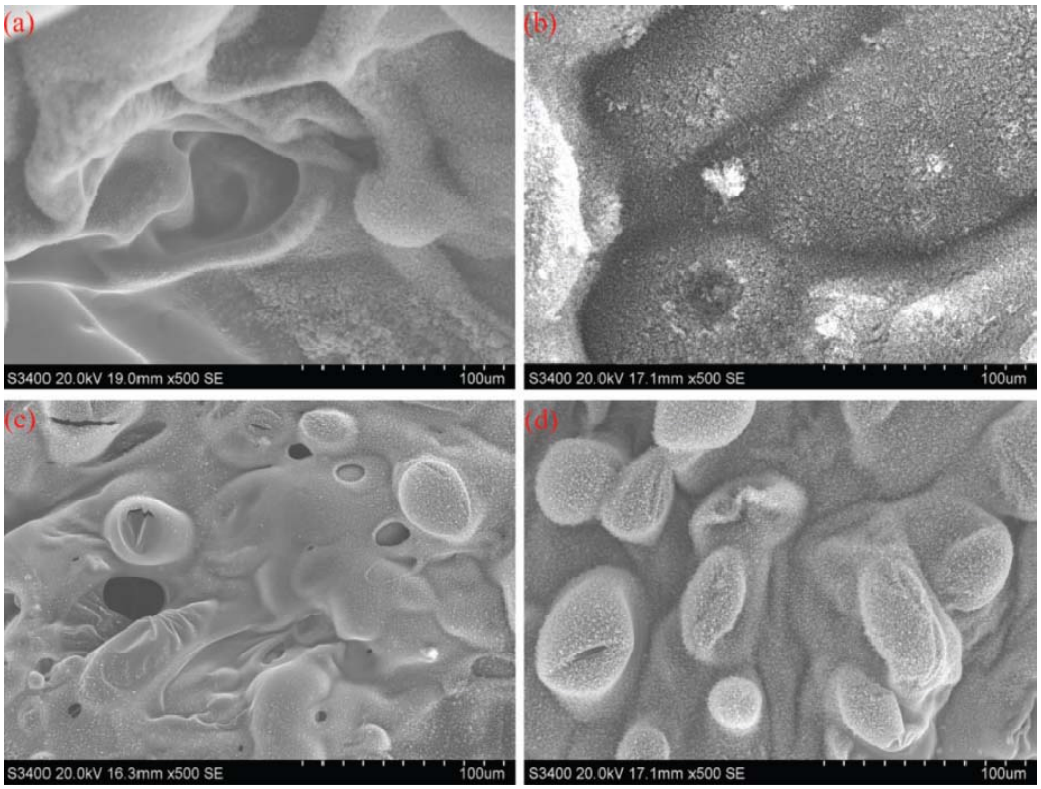

Fig.6.11 Residual char morphologies of different samples, (a) EP-0, (b) EP-B, (c) EP-3, (d) EP-4. EP: epoxy.

6.4 Conclusions

In this chapter, the novel P and N containing compound PMXSPB was synthesized successfully and used as a flame-retardant and curing agent to prepare flame retarded EP resin composites. The EP resin composites filled with PMXSPB exhibited excellent flame resistance and mechanical properties. The flame resistance and char yields of flame-retarded EP resins increased with increasing PMXSPB content. The composite filled with 3.02% phosphorus (EP 100 g and PMXSPB 35 g) had

excellent combination properties. The tensile and impact strengths were 51 Mpa and 4.8 kJ/m^2, respectively, the LOI value was 31.2, the composite passed the UL 94 V-0 test, and the Tg value was 147°C. Compared with BPAODOPE, a novel phosphorus containing flame retardant and curing agents synthesized in our previous work, PMXSPB has a higher phosphorus content per unit mass, a lower fraction of assistant curing agent, and a much higher flame resistance efficiency. In addition, the morphologies of the residual char layer of PMXSPB flameretarded EP show much more numerous and lager bubbles than BPAODOPE, further indicate the intumescent flame resistance mechanism of PMXSPB. As a novel reactive flame-retardant and curing agent, PMXSPB has the potential to be industrialized in the near future.

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Chapter 7

Synthesis of intumescent flame retardant PPSDB and its application in polyethylene

7.1 Introduction

Polyethylene (PE) is widely used in many fields such as packaging, textiles, household goods and electric cable for its excellent electric insulation, great recyclability, good chemical resistance, ease of processing and low cost, and so on [1, 2]. However, inherent flammability and low limited oxygen index (LOI) have restricted its widespread application in some fields where better flame resistance is required. Therefore, improving the flame resistance of PE has become a recent focus of polymer research. As is well known, flame-retardant PE composite can be prepared by mixing flame-retardant additives with resin granules or powders. In those effective flame retardants for PE, halogen-containing compounds areoutstanding flame-retardant additives, especially when compounded with antimonytrioxide [3-6]. Unfortunately, some halogen-containing compounds have beenforbidden for use in many public places due to the release of toxic and corrosivegases which can choke people exposed to the fumes. The gases also corrode the metal equipment and pollute the environment [7-11]. Environment protecters have resisted the large-scale use of halogen-containing flame retardants and advocated the wide application of alternative chemical products [12]. So, halogen-free flame retardants such as intumescent flame-retardant (IFR) systems have been developed rapidly and widely applied in the field of flame-retardant polymers, especially in polyolefin due to their advantages of low smoke, low toxicity, no corrosion [13-15] and higher flame resistance efficiency. Typically, IFR plays an effective flame

resistance role mainly by the condensed-phase mechanism [16-19]. Foam char layers are often formed on the surface of the burning substance during combustion. The char layers act as an insulator and shield the polymers underneath from the heat and also serve as a diffusion barrier to slow down the gasification and vaporization of polymers [20]. Commonly used IFR consists of two or three kinds of flame retardants corresponding to the acid source, carbon source and gas source. It is hard to obtain the best ratio to achieve the best flame resistance; moreover, the mixtures of IFR will deteriorate the mechanical properties due to the poor compatibility.

Recently, some new flame retardant containing phosphorus (P) and nitrogen (N) [21-23], or P, N and silicon (Si) [24], was synthesized to improve the flame resistance efficiency and compatibility with the polymer matrix. Other researches [25, 26] have demonstrated that boron (B)-containing compound greatly improves the flame resistance efficiency and reduces the toxicity of halogen-containing flame retardant. However, flame retardants containing P, N and B elements have not been reported until now. To integrate much more flame resistance elements, a novel intumescent flame retardant of poly(phenylphosphamide spirocyclic diethanolamine borate) (PPSDB) containing P, N and B elements was designed and synthesized successfully by a nucleophilic addition reaction. The structure of PPSDB was characterized by Fourier transform infrared spectrum (FTIR) and nuclear magnetic resonance (^{1}H-NMR). Acting as an intumescent flame retardant, PPSDB was used to prepare PE/PPSDB composites with different fractions, and the thermal performances, flame resistance, mechanical and residue morphology of those composites were studied in detail.

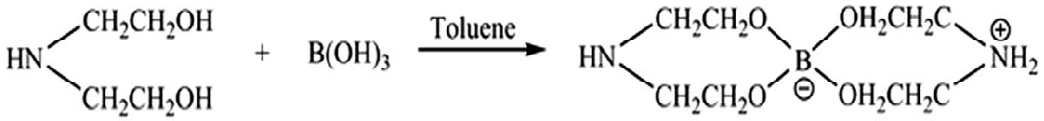
7.2 Experiment

7.2.1 Materials

Polyethylene (PE) was provided by CSPC Petroleum Chemical Industry CO., LTD (Guangdong, China); diethanolamine was purchased from Chinese Medicine Group Chemical Reagent Corp. (Shanghai, China); toluene, acetonitrile, tetrahydrofuran and dichloromethane were supplied by Tianjin Damao Chemical Reagent Factory (Tianjin, China); boric acid was obtained from Shantou Xilong Chemical Co., LTD (Guangdong, China); phenylphosphonic dichloride (PPC) was supplied by Rizhao Lideshi Chemical Co., LTD (Shandong, China).

7.2.2 Synthesis of DEAB

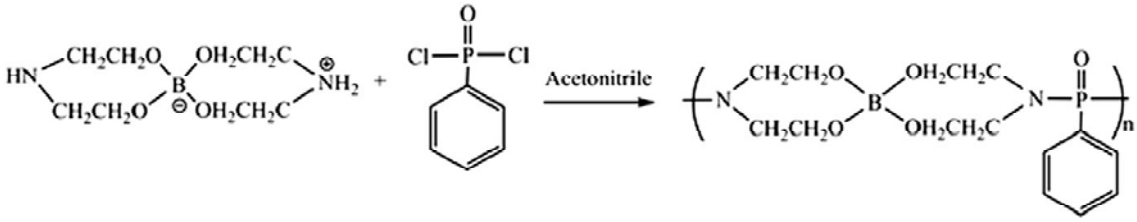
A 250 ml three-necked round bottom flask equipped with a magnetic stirrer, reflux condenser, thermometer and water knockout vessel was placed into a water bath. 24.7 g (0.4 mol) boric acid, 92.5 g (0.88 mol) diethanolamine and 100 ml toluene were added and stirred at 110°C until no water was generated in the reaction system. Then, the reaction mixture was cooled to room temperature slowly, toluene was removed by vacuum distillation and a pale yellow viscous liquid was obtained. Finally, the yellow liquid was refined by washing with tetrahydrofuran (THF) repeatedly. After the refined product was dried at 50°C in vacuum for 12 h, a white liquid was obtained and named as diethanolamine borate (DEAB). The yield of the DEAB product was 85.3 %. The whole reaction equation is illustrated in Scheme 7.1.



Scheme 7.1 Synthesis route of DEAB

7.2.3 Synthesis of PPSDB

21.8 g DEAB (0.1 mol) and 150 ml acetonitrile were taken in a 250 ml flask equipped with a stirrer, thermometer, dropping funnel and circumference condenser. 19.5 g phenylphosphonic dichloride (0.1 mol) was dissolved in acetonitrile to form a homogeneous solution. The solution was poured into the flask and reacted for 1 h at a temperature of 15-20°C. After the reaction was complete, the final mixture was refluxed for 6 h, followed by cooling, filtering, washing and drying. White powders were obtained and the yield was 65.34 %. The specific reaction equation is shown in Scheme 7.2.



Scheme 7.2 Synthesis route of PPSDB

7.2.4 Preparation of flame-retardant PE/PPSDB composites

All the composite samples were prepared by mixing PE and PPSDB in an open mill at 170°C for 15 min. After the composites were mixed uniformly, the composite samples were hot pressed under 10 MPa at 170°C for 5 min and cold pressed under 10 MPa at room temperature for 3 min, then cooled to room temperature. The specimens

were prepared finally.

7.2.5 Characterization

FTIR (NICOLET 470) was used to characterize the chemical structure of DEAB and PPSDB. The ^{1}H NMR (BRUKER AVANCE III) was applied to characterize DEAB and PPSDB with DMSO as a solvent. Thermogravimetric analyzer (STA 449C) was used, and the test temperature ranged from ambient to 800°C at a heating rate of 10°C/min under nitrogen, and the sample's weight was about 10 mg in each test. Scanning electron microscopy (SEM JSM-6360LV) was used to investigate the char surface of flame-retardant PE. The surface of char residues was clad with gold before SEM scanning, and the char residues were obtained from the burned samples in the vertical burning test. Oxygen index instrument (JF-3) was used to measure the limited oxygen index (LOI) of samples with the dimensions of 130×6.5×3 mm^3 according to ASTM D2863-97. The vertical burning tests (UL 94) were performed in CZF-3 horizontal and vertical burning test instrument with sample dimension of 130×13×3 mm^3 according to ASTMD3801. The tensile and impact behavior tests were carried out in TCS-2000 tensile test equipment and GT-7045-MDL digital impact tester according to ASTM D638 and ASTM D256, respectively, and the listed data were the mean of five samples.

7.3 Results and discussion

7.3.1 Characterization of DEAB and PPSDB

The structure of DEAB was characterized by FTIR and shown in Fig. 7.1. The peaks at 3382 and 1637 cm^{-1} corresponded to the stretching vibration and bending vibration of -NH, respectively. The stretching vibration of -CH_2 is observed at 2937 and

2877 cm^{-1}. The peak at 1455 cm^{-1} is assigned to -CH bending vibration. Furthermore, the peak at 869 cm^{-1} is the characteristic absorption peak of the B-O bond. In addition, the structure of DEAB is also characterized by ^{1}H-NMR spectrum and illustrated in Fig. 7.2. The peak at 3.38 and 3.89 ppm are assigned to the proton of -NH and -NH_2, respectively. The peak at 3.68 ppm is associated with -CH_2 protons near the spirocyclic boron. The peak at 2.75 ppm is assigned to the proton of -CH_2 out of the spirocyclic boron. The peak at 7.24 ppm comes from the solvent. These results confirm that the chemical reaction takes place as in Scheme 7.1.

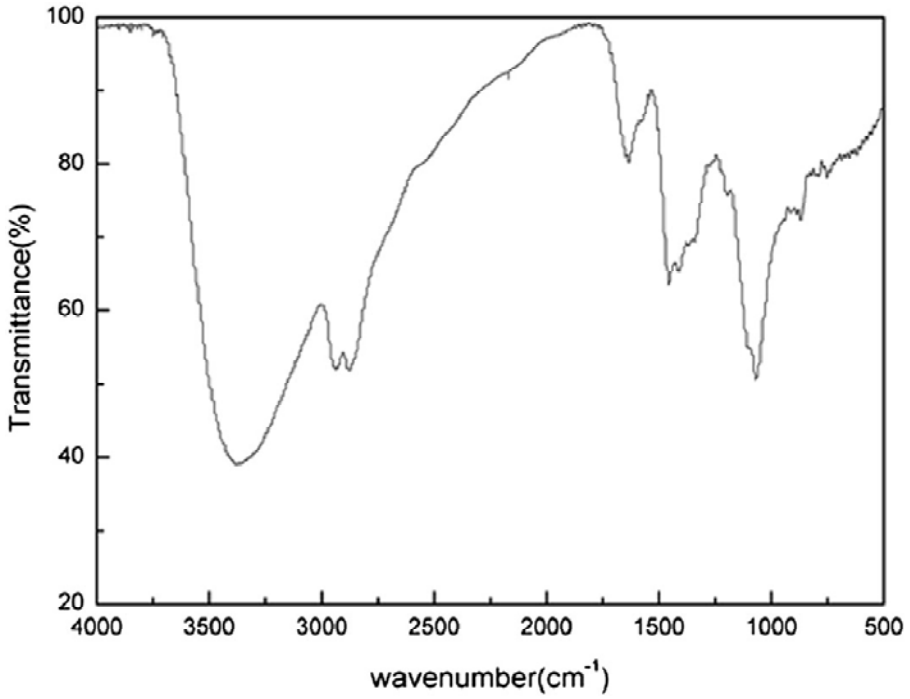


Fig.7.1 FTIR spectrum of DEAB

The structure of PPSDB was characterized by FTIR and is illustrated in Fig. 7.3. The stretching vibration of -NH is observed at 3375 cm^{-1}. The absorption at 2965 and 2809 cm^{-1} is assigned to the stretching vibration of -CH_2. The peak at1359 cm^{-1} is associated with the stretching vibration of -CN. The peaks at 1613, 1586 and 1425 cm^{-1} are assigned to the skeleton vibration from the benzene ring. The absorption peak of

P=O is observed at 1247 cm^{-1}. Moreover, the peak of 961 cm^{-1} is associated with the stretching vibration of P-N, which indicates thatthe final product was obtained successfully. The ^{1}HNMR spectrum of PPSDB is shown in Fig. 7.4.

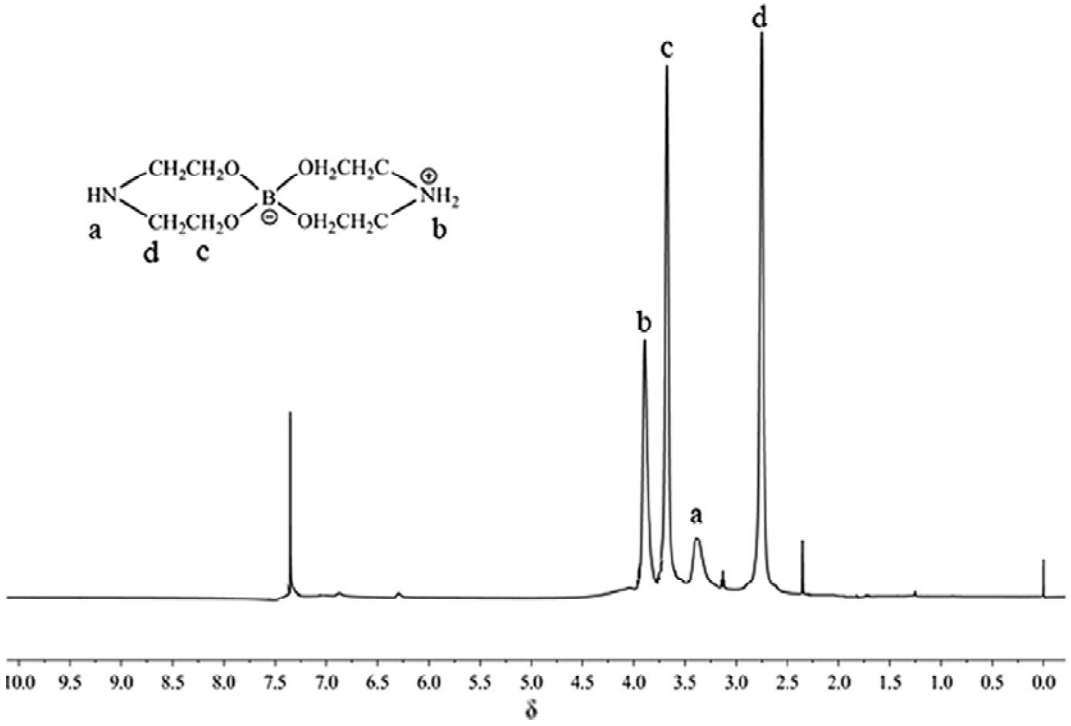


Fig. 7.2 ^{1}H-NMR spectrum of DEAB

The multiple peaks between 7.54 and 7.81 ppm belong to the benzene ring. The signal at 3.65 ppm is attributed to the -CH_2 protons adjacent to the spirocyclic boron. The peak of -CH_2 protons out of the spirocyclic boron is observed at 2.98 ppm. The peak at 8.66 ppm is associated with P-NH, which confirms the final structure of PPSDB. The peaks at 3.36 and 2.48 ppm belong to the water protons and protons of the DMSO solvent, respectively. The chemical shifts of the absorption peaks and the area ratios of the peak integration are identical to the expected chemical structure.

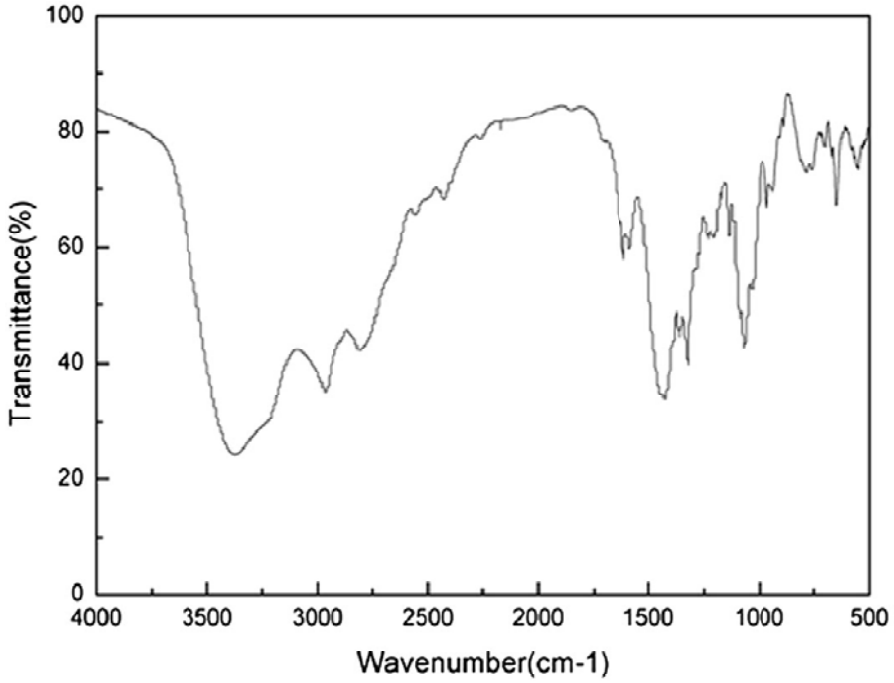


Fig. 7.3 FTIR spectrum of PPSDB

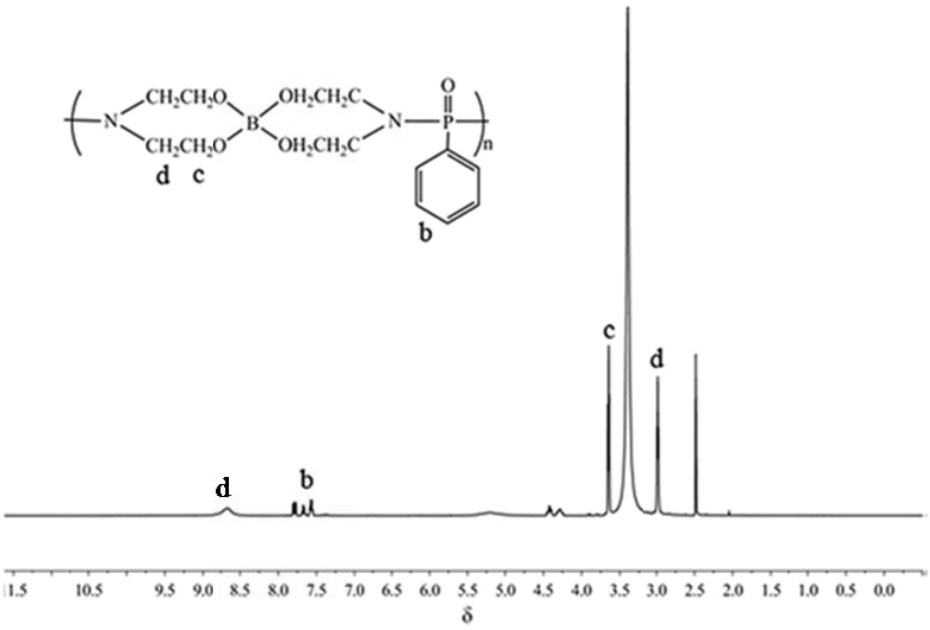


Fig.7.4 ^{1}HNMR spectrum of PPSDB

7.3.2 Flame resistance of PE/PPSDB composites

Limiting oxygen index (LOI) and vertical burning test (UL 94) are widely used to evaluate the flame resistance of polymer composites. LOI is defined as the minimum percentage of oxygen in an oxygen-nitrogen mixture, which is just sufficient to sustain combustion (after ignition) of the specimen. The sample can be considered as a flame-retardant material when the LOI value is more than 26. UL 94 test results fall into three categories, with burning ratings V-0, V-1 and V-2, and the V-0 rating corresponds to the highest level of flame resistance. The LOI values and vertical burning ratings of pure PE and PE/PPSDB composites are shown in Table 7.1.

Table 7.1 Flame resistance of PE and PE/PPSDB composites

Samples	LOI, %	UL 94 rating	
		Ratings	Dripping
PE	17.4	Fail	Yes
PE/10 % IFR	21.3	Fail	Yes
PE/15 % IFR	23.1	Fail	Yes
PE/20 % IFR	24.9	V-2	Yes
PE/25 % IFR	27.5	V-1	No
PE/30 % IFR	29.2	V-0	No

Pure PE is highly combustible with molten drips, the LOI value is only 17.4 and UL-94 can not reach any rating. Compared with pure PE, the PE/PPSDB composites show a better flame resistance performance. The LOI values of flame-retardant PE/PPSDB composites improve obviously with an increase of the PPSDB fraction. When the PPSDB fraction is 30 wt% in composite, the LOI value is 29.2, the increment of LOI (DLOI) is 11.8 when compared with pure PE, the UL 94 V-0 rating can be

achieved, and there are no molten drips during vertical burning (UL 94 test) when the PPSDB content is more than 25 wt% in the composite. So the novel IFR PPSDB shows higher flame resistance efficiency and excellent anti-dripping property. The reason for PPSDB's better flame resistance is attributed to the combination of P, Nand B elements and the special molecular structure in Scheme 7.2.

When PE/PPSDB composite burns at a lower temperature, the P=O bonds provide the acid resource, the rigid phenyl groups connecting P=O play an anti-burning effect to a certain extent, the N element would turn into incombustible NH_3 and the B element will bechanged into B_2O_3 or boric acid. The intermediate or final products of P, N and B elements prevent the composite from burning further, and the synergetic effect of three effective elements can be achieved to improve the flame resistance efficiency of PE/PPSDB composites prominently.

7.3.3 Thermal stability

Table7.2 Date of TGA curves for PPSDB and PE/PPSDB at a heating rate of 10°C/min

Sample	T_i(°C)	$T_{50\%}$ (°C)	Residue at 800 (%)
PE	420	470	1.00
PPSDB	254	339	25.1
PE-10 % IFR	343	475	1.52
PE-15 % IFR	310	478	2.43
PE-20 % IFR	286	476	3.21
PE-25 % IFR	266	473	5.2
PE-30 % IFR	250	475	6.87

T_i the initial decomposition temperature, $T_{50\%}$ the temperature of 50 wt% weight loss

Thermogravimetric analysis (TGA) is a common technique for evaluating the thermal stability of various polymers, and it also indicates the decomposition behaviors of the polymer at various temperatures [27, 28]. The TGA curves of PPSDB and PE/PPSDB composites are shown in Fig.7.5, and the corresponding data are listed in Table 7.2.

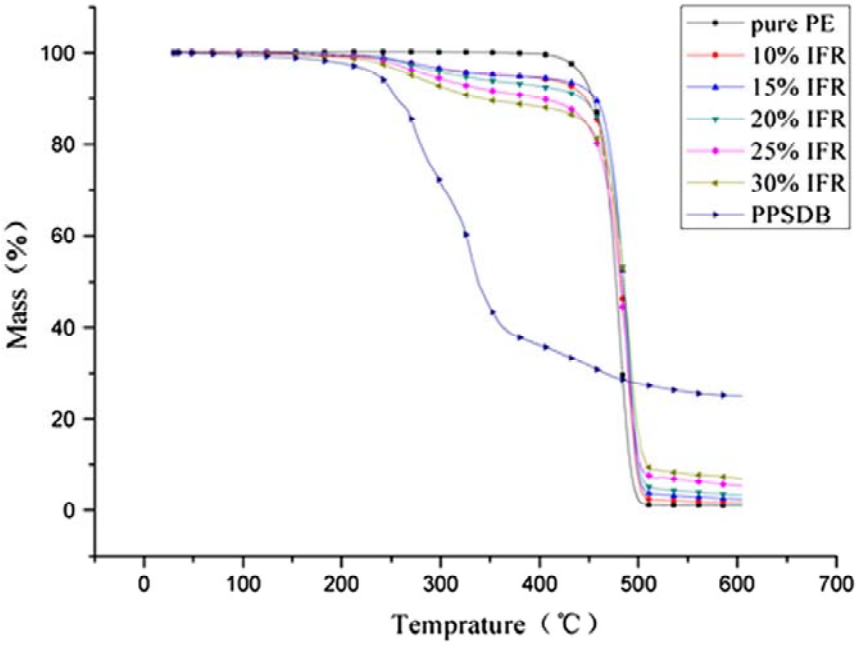


Fig. 7.5 TGA curves of the PPSDB and PE/PPSDB composites

The initial decomposition temperature of PPSDB is 254°C; the weight loss increases rapidly with an increase of temperature. The initial decomposition of PPSDB at a lower temperature is assigned to the weak boron spiro bonds. Two degradation steps of PPSDB are observed at about 260 and 350°C, respectively. The major degradation between 260 and 350°C is attributed to the scission of boron spiro bonds. The subsequent minor degradation is observed at atemperature ranging from 350 to 470 °C, which is considered as that for the formation of residue char. The weight loss slows down when the temperature is higher than 500°C, and the final residue is 25.1 %

at 800 °C. Generally speaking, the common processing temperature of PE is about 200°C, and the initial decomposition temperature and thermal stability of PPSDB can meet the requirement for fabricating the PE/PPSDB composite sufficiently. For pure PE, the initial degradation temperature and the maximum decomposition temperature is 420 and about 470°C, respectively. When the temperature is higher than 500°C, the weight will not decrease any longer and the char residue is negligible (only 1.0 %). For the PE/PPSDB composites with different fractions of flame retardant, all the initial degradation temperatures are lower than pure PE, which is attributed to the weaker thermal stability of PPSDB, as the B-O, P=O and C-N bonds in PPSDB are less stable than uniform C-C bonds in PE. For the PE/PPSDB composites, the decomposition curves are similar in shape, the initial decomposition temperatures are higher than 250°C, and the maximum weight loss temperatures range from 450 to 500°C. When the temperature is higher than 510°C, the weight lossshows no obvious change, which indicates that the char residues remain constant and the composites decompose completely. We can also find that the char residues of PE/PPSDB composites increase with an increase of the PPSDB fraction, which is attributed to the formation of the char layer induced by PPSDB.

According to the thermal decomposition curves and the molecular structure of PPSDB, we attempt to illustrate the flame resistance mechanism of PPSDB in the composite. At a lower temperature, the P=O bonds or B-O bonds of PPSDB will decompose and generate inorganic acid, such as phosphoric acid, metaphosphoric acid or boric acid. Esterification reaction would take place between inorganic acid and carbon source, and the carbon source would turn into the char layer after the dehydration reaction. Then, at a higher temperature, the polymer matrix will be molten,

and the polymer melt expands by bubbles formed by the water vapor or NH_3 from gas source (C-N bonds). The inflammable gas can also serve as catalyst for the esterification reaction. Finally, the whole system change from gel into compact porous char layers on the surface of the sample, which prevents the composite from decomposing further and isolates the heat and oxygen from the surroundings. That is the condensed-phase mechanism of flame resistance.

7.3.4 Mechanical properties

Table 7.3 Mechanical properties of PE and PE/PPSDB composites

Sample	Tensile strength (MPa)	Impact strength (kJ/cm^2)
PE	25.5	15.5
PE/PPSDB-10%	26.2	10.9
PE/PPSDB-15%	25.3	9.4
PE/PPSDB20 %	24.9	11.2
PE/PPSDB25 %	20.8	12.1
PE/PPSDB30 %	18.6	12.5

The mechanical properties of PE and PE/PPSDB composites are shown in Table 7.3. The results show that the mechanical properties of composites decrease with an increase of the PPSDB fraction. It can be seen that the tensile strength of the PE/PPSDB composite with 10 wt% PPSDB increases to 26.2 from 25.5 MPa of pure PE, and the corresponding impact strength drops to 10.9 from 15.5 kJ/m^2 of pure PE. When the fraction of PPSDB is more than 10 wt%, the tensile strength decreases and the notched impact strength of composites improves with an increase of the PPSDB fraction. Considering the flame resistance, the PE/PPSDB composite with 30 wt% PPSDB has

much more practical significance, and the tensile strength and notched impact strength are 18.6 MPa and 12.5 kJ/m^2, respectively. Compared with metal hydroxide or mixtures of intumescent flame retardants, the PPSDB integrates the P, N and B elements by forming the non-polar phenyl andspirocyclic groups, which play a positive effect in improving the flame resistance efficiency and compatibility between the flame retardant and PE matrix [5].

7.3.5 Morphologies of the char residue

Fig.7.6 shows the microscopic morphologies of char layers. The specimen for SEM is the final residue of the sample PE/PPSDB-30 wt%. There are some protruding structures on the smooth char layer surface. After the sample is magnified by 1000 times, the protruding structure is composed of many small protuberances, which are just generated by the bubbles of inflammable gas. The special structure with lots of protuberances in the char layer prevents the composites from burning further and enhances the anti-dripping property effectively, which proves the condensed-phase mechanism of novel flame resistance PPSDB.

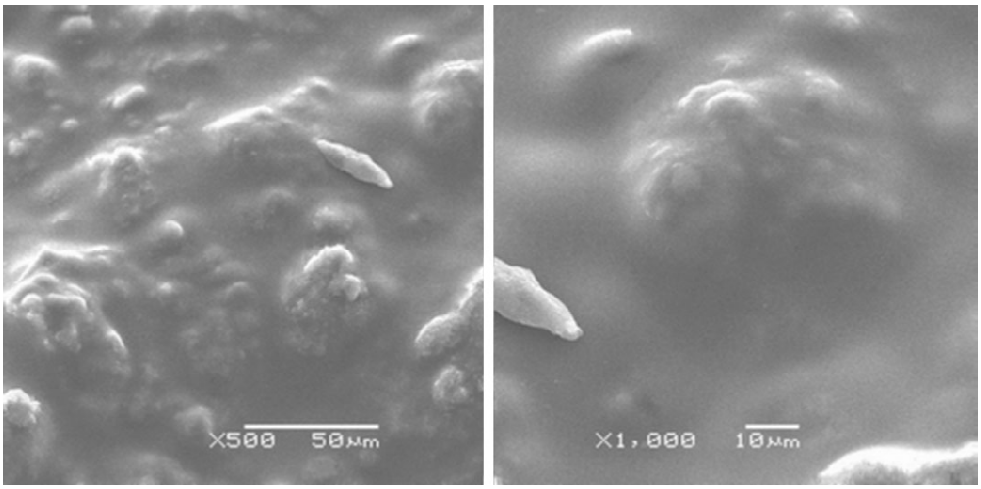


Fig.7.6 SEM micrographs for the char residue after vertical burning of PE/PPSDB-30 %

7.4 Conclusions

A novel flame retardant (PPSDB) containing phosphorus, nitrogen and boron was synthesized successfully and its chemical structure was confirmed by FTIR and ^{1}HNMR. The thermal stability of PPSDB was confirmed to meet the requirement for fabricating PE composites by TGA, and the initial decomposition temperatures of PE/PPSDB composites decreased and the char residue increased with an increase of PPSDB fraction. PE/PPSDB composites showed good flame resistance, antidripping properties and compatibility. When the PPSDB fraction was 30 wt% in the PE/PPSDB composite, the LOI value was 29.2, vertical burning reached UL 94 V-0 rating, and the tensile strength and notched impact strength were 18.6 MPa and 12.5kJ/m^2, respectively. The morphologies of char residue showed a lot of protruding structures consisting of smaller protuberances, which prevented the combustion of the composite and enhanced the anti-dripping property effectively. The PPSDB integrated the P, N and B elements by forming the non-polar phenyland spirocyclic groups, which has a positive effect in improving the flame resistance efficiency and the compatibility between the flame retardant and PE matrix. It has a potential to be industrialized in the near future.

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Conclusions

Epoxy resin is a kind of high performance polymer materials. Epoxy resin based composites are widely applied in various areas due to their low cost, ease of fabrication. However, the commonly-used epoxy resins are consists mainly of carbon, hydrogen and oxygen atoms, therefore, there are some shortages, the high flammability and low thermal stability at elevated temperatures. In order to enhance the flame resistance of epoxy resin, flame retarded epoxy resins were prepared by adding additive halogen free flame retardants or reactive flame retardants to improve the flame retardance of epoxy resin. In this paper, some novel flame retardants or compound flame retardants were attempted to be synthesized or prepared to enhance the flame resistance and mechanical performance of flame retarded polymer composites.

In the seond chapter, MRP was synthesized through in-situ polymerization method and characterized by XPS and SEM, it was used as a synergistic agent for MH and ATH. Flame retarded PE composites were prepared successfully with MH/ATH/MRP compound flame retardants. The best ratio of compound flame retardants of MH/ATH/RP was testified as 46/46/8, when filling with 45wt% compound flame retardants as above ratio, the prepared PE composite had a better combination properties, tensile strength was 10.3 MPa, impact strength was 13.5 kJ/m^2, the LOI was 29.1, vertical burning reached UL 94 V-1 rating. In order to improve the mechanical properties further, two polymeric compatibilizers POE-g-MAH and EPDM-g-MAH were used to toughen the composite. The results showed that the addition of compatibilizer improved the flame resistance and mechanical properties of composite greatly. POE-g-MAH had higher contribution in flame resistance, and EPDM-g-MAH had a better toughening effect under the same circumstance. Considering the

cost/performance ratio, the flame retarded PE composite filling with 10 wt% EPDM-g-MAH had the best performance, LOI was 29.5, vertical burning reached UL 94 V-0 rating, tensile strength and elongation at break were 11.7 MPa and 105.4%, impact strength was 22.8 kJ/m^2. The recipe of flame retarded PE composite can be applied in non-halogen flame retarded cables or other relative products.

In the third chapter, a novel aryl phosphinate dianhydride BPAODOPE was synthesized successfully, and used as hardener and flame retardant for preparing halogen-free flame retarded epoxy resins when coupled with another curing agent. The epoxy resin composites filling with BPAODOPE had excellent flame resistance and higher char yield, and the flame resistance and char yields of the flame retarded epoxy resins increased with an increase of phosphorus content. And the epoxy resins with the phosphorus contents of 1.75% showed excellent combination properties. The results also show that BPAODOPE has some shortcomings, it has a lower phosphorous content, when the phosphorous content is 2.25%, the mechanical properties of epoxy resin will decrease obviously, tensile strength and impact strength of the sample were 73.5% and 54.95% for their values of neat epoxy resin respectively. So the further study will focus on the synthesis of some novel reactive flame retardants, which should have a higher phosphorous content of unit mass, and improve the combination properties of flame retarded epoxy resins.

In the fourth chapter, a novel phosphorus containning flame retardant and curing agent PES was synthesized successfully with pentaerythritol, phosphorus oxychloride and ethylenediamine, the structure and performance of production was characterized by using FTIR, ^{1}HNMR, ESI-MS and TG. The synthesized PES and DDS was used as flame retardant and curing agent, and the flame retarded epoxy resin composites were

prepared with different phosphorus content. The TG results showed that the addition of PES decreased the initial decomposition temperature of epoxy resin, and the residual char of composites increased with an increase of PES fraction at 800℃. The residual char suface of flame retarded composite was observed by SEM, and the results show that the swell and compact char lay can be formed after the filling of PES. The flame retarded composite with the phosphorous content of 3.48% shows the best combination performance, the limited oxygen index increases from 20.3 to 28.9, and reaches UL 94 V-0 rating, the tensile strength and impact strength of this sample are 62.76 Mpa and 6.81kJ/m^2 respectively. Although the addition of PES weaken the mechanical performance of composite, it can greatly improve the flame retardance of epoxy resin, considering the combination performance of flame retarded composite, the synthesized phosphorus containning PES has a promising application prospect.

In the fifth chapter, the research demonstrated PDEPDM flame retardant was prepared successfully by three step reactions. And the PDEPDM was charactered by the FTIR, NMR and TG. In order to obtain high purity of the PDEPDM, the suitable reaction conditions needed to be controlled, such as reaction temperature, reaction time and solvent ratio, fabrication conditions were optimized, shown as the follows: reaction temperature was 85^{o}C, reaction time was 5 h and the solvent ratio of the n_{MA} and n_{PDCEPE} was 2.1:1, it was also studied the flame performance, the PDEPDM was added into the polypropylene, and the performance of the flame retardant was researched by LOI and UL 94 rating. When the 32% PDEPDM was filled, the flame properties can achieve V-0 rating and the tensile strength and impact strength were 10.06 MPa and 16.77 kJ/m^2.

In the sixth chapter, the novel P and N containing compound PMXSPB was

synthesized successfully and used as a flame-retardant and curing agent to prepare flame retarded EP resin composites. The EP resin composites filled with PMXSPB exhibited excellent flame resistance and mechanical properties. The flame resistance and char yields of flame-retarded EP resins increased with increasing PMXSPB content. The composite filled with 3.02% phosphorus (EP 100 g and PMXSPB 35 g) had excellent combination properties. The tensile and impact strengths were 51 Mpa and 4.8 kJ/m^2, respectively, the LOI value was 31.2, the composite passed the UL 94 V-0 test, and the Tg value was 147°C. Compared with BPAODOPE, the novel phosphorus containing flame-retardant and curing agents synthesized in our previous work, PMXSPB has a higher phosphorus content per unit mass, a lower fraction of assistant curing agent, and a much higher flame resistance efficiency. In addition, the morphologies of the residual char layer of PMXSPB flame retarded EP show much more numerous and lager bubbles than BPAODOPE, further indicating the intumescent flame resistance mechanism of PMXSPB. As a novel reactive flame-retardant and curing agent, PMXSPB has the potential to be industrialized in the near future.

In the last chapter, a novel flame retardant (PPSDB) containing phosphorus, nitrogen and boron was synthesized successfully and its chemical structure was confirmed by FTIR and ^{1}HNMR. The thermal stability of PPSDB was confirmed to meet the requirement for fabricating PE composites by TGA, and the initial decomposition temperatures of PE/PPSDB composites decreased and the char residue increased with an increase of PPSDB fraction. PE/PPSDB composites showed good flame resistance, anti-dripping properties and compatibility. When the PPSDB fraction was 30 wt% in the PE/PPSDB composite, the LOI value was 29.2, vertical burning reached UL-94 V-0 rating, and the tensile strength and notched impact strength were

18.6 MPa and 12.5kJ/m^2, respectively. The morphologies of char residue showed a lot of protruding structures consisting of smaller protuberances, which prevented the combustion of the composite and enhanced the anti-dripping property effectively. The PPSDB integrated the P, N and B elements by forming the non-polar phenyl and spirocyclic groups, which has a positive effect in improving the flame resistance efficiency and the compatibility between the flame retardant and PE matrix. It has a potential to be industrialized in the near future.

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